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THE STRENGTH OF PLASTICS AND GLASS

A Study in Time-Sensitive Materials

THE STRENGTH OF PLASTICS AND GLASS

A Study in Time-Sensitive Materials

By

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With 108 Diagrams
and 16 Plates

LONDON
CLEAVER-HUME PRESS LTD
NEW YORK: INTERSCIENCE PUBLISHERS INC.

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First published 1949

PRINTED IN GREAT BRITAIN
BY UNWIN BROTHERS LTD
LONDON AND WOKING

PREFACE

THIS book is primarily concerned with the mechanical properties of plastics and glass. The author hopes, however, that it may prove of interest not only to engineers and scientists working on those materials, but, owing to the fundamental nature of some of the problems discussed, to many outside that specialized field who are interested in the general properties of matter and the experimental and mathematical technique of their investigation. The subject is one where the interests of different sciences meet and is therefore a field in which the present inevitable specialization in the training of a scientific worker tends to be unsuitable. This makes the writing of a monograph both more difficult and more necessary.

The types of material discussed show a wide variation in their properties. They range from rigid, brittle glasses capable of only slight deformations, to tough and flexible plastics. The mechanical behaviour of all these materials has been the subject of much recent research and the broad outline of many of the observable phenomena is now fairly clear. On the other hand the proper theoretical explanations are often in doubt and the writer has therefore placed the main emphasis on the presentation of facts and, in general, has only given the theories as far as they have been accompanied by experimental work. A good deal of the modern theory of visco-elastic behaviour has therefore been omitted. However, within the framework of established knowledge, an attempt has been made to emphasize the importance and interest which attaches to problems concerning the interrelation of mechanical properties. This leads to the presentation, at the beginning of Chapter VI, of the writer's views on some of the major factors influencing impact strength. The modern theory of rubber elasticity is also shortly described and a number of examples are given which illustrate the behaviour of rubbers. It is considered that these references are necessary owing to the close connection which exists between all materials showing deformations of the highly elastic type, but a discussion of the mechanical properties of rubbers is not one of the particular objects undertaken here.

In fairness to his former employers it should be stated that this work was commenced when the writer was employed by Messrs. Colmore Adhesives Limited and their associates the Tyneside Safety Glass Co., Ltd., and that where his own work is quoted it was carried out as part of their research programme. The author would also like to express his thanks to the many friends who have discussed parts of the work with him and particularly to Dr. L. R. G. Treloar who read through the work in typescript and made many valuable suggestions. He is also indebted to his publishers for their continuous advice and assistance during the work of publication.

R. N. HAWARD

MANCHESTER
May 1949

ACKNOWLEDGMENT

A CRITICAL survey such as this could not have been adequately made without permission to reproduce or adapt illustrations from a large number of sources. These are severally indicated by the numbers in the legends referring to lists at the end of the chapters; but the author wishes here to express his gratitude to all those scientists, societies and publishers whose willing help in this respect has been forthcoming.

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NOMENCLATURE

Symbols used in the text on several occasions are listed below.

f	is used for a fracture stress, together with suitable subscripts, e.g. f_T for tensile strength, f_B for bending strength. When a fracture stress at a particular time is intended this is indicated; e.g. $f_{s,t}$ means a shearing strength measured in time, t.
P	a force or load.
E	Young's Modulus of Elasticity.
σ	Poisson's ratio.
l	the length of a test piece.
γ	surface tension.
ρ	specific gravity.
τ	relaxation or "orientation" time.
v	volume.
D	a deformation of mixed or unspecified type.
D_{OE}	the ordinary elastic or ideal Hookean deformation.
D_{HE}	the highly elastic deformation.
D_{visc}	the viscous deformation.
s	the standard deviation of a sample.
v	coefficient of variation of a sample.
V	velocity.
M	molecular weight.
W	weight of the striker in an impact experiment.
w	weight of the test-piece in an impact experiment.

CHAPTER I

STRENGTH RELATIONS

THIS work is concerned with the strength of plastic materials and glasses. Its object is to present the various quantities involved in the deformation and fracture of these materials and to discuss the relations between them. From the point of view of strength relations it is essential to appreciate that many different quantities having different dimensions are grouped under the heading of strength; the results of such measurements may be presented in terms of a stress $(ML^{-1}T^{-2})$, a strain (zero dimensions), or an energy $(ML^{2}T^{-2})$. Naturally, many other quantities have been and will continue to be recorded which do not belong to any of these groups, particularly where the behaviour of the material cannot be adequately or conveniently dealt with in theoretical terms, but we may consider these three types of measurement and emphasize the essential distinctions between them.

In discussing the various relations between mechanical properties, it is assumed throughout that only similar quantities with similar dimensions should be directly compared. It may be possible in a particular case to find a definite correlation between a stress, e.g. a bending strength, and an energy, e.g. an impact measurement, but where such correlations occur it must be assumed either that other relevant factors are not changing sufficiently to affect the correlation, or, alternatively, that they are mutually cancelling out. Any full theory must bring in the missing elements connecting definite types of measurement even though variations in them may later prove to be negligible in particular cases.

Energy absorption is generally regarded as being derived from the other two fundamental quantities, namely: fracture stress (static strength) and deformation. For instance, with a material obeying the assumptions of the classical theories of elasticity a stress applied to a given volume of a given shape will lead to a definite strain and to a strain energy proportional to the volume $(ML^{-1}T^{-2} \times L^{3} = ML^{2}T^{-2})$. However, plastic materials in general disobey the classical theories of elasticity and many difficulties arise therefrom. For this reason, the inclusion of *massive glass*, whose elastic behaviour closely corresponds with that of an ideal isotropic solid in the same work, often gives a basis of comparison, illustrating differences introduced by deviations from ideal elastic behaviour in plastics, and so increases the generality of our approach. An important element in the subject of strength is that of the existence of *parallel* properties, that is, properties which all change in the same way when a variation is made, either in the material itself or in the conditions of measurement; false correlations are readily obtained which derive not from the nature of the quantities measured, but from casual similarities pertaining to a particular group of materials. In this way properties may become vague and incapable of precise definition, a state of affairs widely recognized to exist in connection with the subject of hardness and related phenomena. Here the same difficulty arises with metals and the position has been described by Tuckerman:[1]

> Hardness in common parlance represents a hazily conceived conglomeration or aggregate of properties of a material more or less related to each other. These properties include such varied things as resistance to abrasion, resistance to scratching, ability to cut other materials, resistance to plastic deformation, high modulus of elasticity, high yield point, high strength, absence of elastic damping, brittleness, lack of ductility and malleability, high melting temperature, magnetic retentivity, etc. This confusion under the designation "hardness" results from the fact that there is a rough parallelism in these properties in a large number of materials. The fact that "hardness" thus conceived is a conglomeration of different, more or less unrelated properties makes it impossible to correlate any one definite, measurable property with all the current implications of hardness. This does not mean that under the hazy conglomeration of properties which are included in the common understanding of hardness, there are not included very important properties of the material.

The existence of these roughly parallel tendencies, for instance between elastic modulus and tensile strength, occurs with plastics just as with metals and may equally lead to circumstances in which a measurement of the wrong property may lead to practically workable results. Nevertheless these differences rapidly become apparent if we attempt to make measurements for quite different materials. For instance, the Brinell hardness test may place a series of plastic materials in approximately the correct order of resistance to scratching, but it cannot be readily applied to glass for the same purpose. With plastics correlation is obtained simply because irreversible deformations, breaking stresses, and elasticity in general all change in a roughly similar way with different conditions and materials; but massive glass irreversible deformations not entailing rupture are almost impossible to measure at ordinary temperatures and consequently tests cannot be based upon them. Naturally it may well transpire that where a series of properties of a material all change in the same direction, say with temperature, this is not mere chance but is connected with certain fundamental similarities in the molecular processes involved. However, apart from some recent work on the properties of rubbers, little has yet been done to establish a firm molecular theory of strength properties, and until the phenomena have been more thoroughly investigated and the various inter-relations cleared up, the theories of strength cannot assume or build upon such connections. On the contrary the aim must rather be to render strength measurements and criteria independent of any undefined internal correlations of properties.

It is important to appreciate that the distinction drawn between the theoretical explanation of phenomena and their empirical description is not necessarily vital in strength relations. If a given strength property enters into another property in somewhat different conditions we can deal with its contribution with whatever accuracy is possible in its prediction. The question of the derivation of whatever relation we use in making predictions is only of interest in so far as it may increase or reduce our confidence in their reliability. For example, the deformation of two materials A and B may be described according to an empirical relation involving powers of the stress and the time. This tells us very little about the processes involved in deformation but it may enable us to say that material A is more easily deformed than B under small stresses and long times, and the reverse occurs at high stresses and short times; we can then proceed to use the materials more intelligently, though we know little about the mechanisms of deformation.

The three basic quantities involved in the theory of strength relations, namely: static strength (or fracture stress), deformation, and energy measurements will now be shortly discussed in turn. Under *static strength* measurements we include all those tests in which the material fails by rupture under an observed stress. These include tensile, shear, bending, and compression tests, as well as certain other cases. In this connection it appears to be commonly accepted that plastics break in tension and in shear. However, a few difficulties should be pointed out, though not very much is known of how they affect the behaviour of plastic materials. Firstly, for any criterion of failure there exists, as pointed out by Hertz,[2] a surface, closed or in part extending to infinity, such that the principal stresses represented by the rectangular co-ordinates X_x, Y_y, Z_z, of any point in the surface can just be borne by the material without exceeding the particular failure limit. All points within the surface can be withstood by the material but points outside will cause failure. The conventionally measured properties of shear and tensile strength will be represented only by particular points on the surface, but, in general, there is no reason to assume that the surface is completely defined by these two measurements. Even if a material is failing under tension applied in a given direction there is no reason to assume that the value of this tensile strength will be independent of stresses operating in other directions.*

Secondly, under different conditions of rupture the deformation, particularly of thermoplastics, may differ very widely; this will considerably complicate the question of static strength and may render certain types of results non-comparable for many purposes. Nevertheless, in the absence of fuller knowledge we deal with the properties of our materials in terms of tension, shear, compression, etc., and assume that in any state of stress the material will fail if one of these exceeds the measured strength values.

Naturally the result of a strength measurement will depend on any change in the conditions affecting the material as a whole, such as temperature or humidity. More recently it has become widely recognized that static strength measurements are dependent on the time allowed for failure to take place. This property occurs characteristically in both plastics and massive glass, and the results differ from those of the high melting point metals such as copper and steel where static fatigue is much smaller.[3]

In *deformation* measurements the importance of time is generally obvious with plastics and must be regarded as diminishing the value of many of the published stress-strain curves. Here there is a marked contrast between the behaviour of most plastics and of massive glass. The latter may be regarded as an ideal isotropic solid whose behaviour is therefore adequately described by the classical theories of elasticity; but with plastics, even where a satisfactory numerical description of deformation is possible, it is exceedingly difficult to apply the relations obtained to any but the simplest test pieces. For example, even the mathematical difficulties in describing the deformation of a simple beam are severe, and the consequences in connection with measurement of flexural strength are important. Thus two materials may have the same tensile strength under all conditions and different bending strengths, but this difference need not be a true difference in static strength under the two conditions but a difference derived purely from variations in deformation. On the other hand certain measurements based on applying a particular deformation to a material may in reality be measurements of static strength.

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* With glass there does seem good reason to believe that rupture occurs only under tension, generally at a surface.

The third main type of strength measurement, that based on *energy*, necessarily involves both deformation and fracture. The most important case, that of impact strength, equally implies short times, but there is also the possibility of making measurements of energy under slow deformation conditions. Here it is natural to try and correlate the results of slow and fast measurements of energy absorption. Glass appears to present few serious difficulties at low velocities of impact, but at higher velocities, where the dynamic deformation of a perfectly elastic solid differs from its static deformation, mathematical difficulties are an important bar to progress and have largely prevented the development of a thorough treatment. An indication of some of these complexities, which are common to all known materials, may be obtained from a discussion by Arnold[4] of the impact stresses in a freely supported beam. With plastics, particularly with the thermoplastics, the behaviour even under slow deformations is so complicated as to render almost any impact measurement "explicable," and we can only exclude a few possibilities as the result of theoretical considerations.

It is therefore to be expected that many of the relations between mechanical properties remain obscure. On the other hand, reference to the case of glass, whose deformation properties under normal conditions are particularly simple, sometimes enables certain relations to be established which may also apply to the case of plastics. In this way it may be possible to simplify the problem of the behaviour of plastic materials to a certain extent or to indicate a line of approach to phenomena which do not, by themselves, allow of any certain explanation. Such considerations, therefore, also furnish a reason for treating the mechanical properties of plastic materials and glasses in a single work.

REFERENCES

(1) TUCKERMAN, L. B.: *Proc. A.S.T.M.*, **38** (1938), p. 211.
(2) HERTZ, H.: *Misc. Papers*, trans. Jones and Schott, pp. 178–83 (Macmillan, New York, 1896).
(3) TIMOSHENKO, S.: *Strength of Materials*, 2nd edition, Vol. II, p. 425 (McGraw Hill, 1941).
(4) ARNOLD, R. N.: *Proc. Inst. Mech. Eng.*, **137** (1937), p. 217.

CHAPTER II

THE STATIC STRENGTH OF PLASTIC MATERIALS

TENSILE strength, bending, compressive and shear strength may be regarded as aspects of the static strength of the plastic materials, i.e. the type of strength measurements in which failure occurs through the application of a steady or slowly increasing stress which has time to distribute itself through the specimen in accordance with the geometry of the test. While the material is being broken a large or small deformation will occur; where this deformation is large the real strength of the plastic at its breaking point may be considerably above the figure generally quoted, calculated on the initial cross-section under load. Under such large deformations the long chain molecules of a plastic commonly become oriented or crystallized so that their length in the direction of application of stress greatly exceeds that to be expected under equilibrium conditions,[1] and their properties may even approach those of fibres. These changes under stress must always be borne in mind in considering the operation of other variables. For instance, the addition of plasticizer not only decreases the tensile strength but may also lead to a greatly increased deformation at break. Nevertheless the customary calculation of the strength of a material on its original cross-section has the justification that when broken in use its dimensions at the point of stressing normally decrease in a similar way.

The four types of test mentioned do not exhaust the subject of breakage under static stress, which should involve all possible arrangements of stress, but it does include practically all the recorded measurements. On the other hand, the four figures obtained from tensile, bending, shear, and compression tests probably do not represent four distinct limiting cases of breakage under differing stress conditions. For example, under bending the test piece will frequently break in tension at the lower surface, and, under compression in one dimension, rupture often takes place under the action of shearing stresses. Thus fracture may take place in two fundamentally different ways, namely: by the separation of planes in response to the tensile component of stress, or by the sliding of planes in response to the tangential component. However, it is not certain that both modes of fracture can be made to occur with all plastic materials, though one may assume that the two types exist until there is evidence to the contrary. Weibull[2] made some experiments designed to test the possible theories of rupture using a brittle plastic and also glass, and he found that the results favoured a maximum stress or strain theory of rupture and definitely excluded the possibility of breakage under shear. This does not prove that these materials could never break under shear in a test in which the shearing forces were relatively larger compared with the tensile forces than they were in Weibull's experiments; nor that because certain bending and compression tests actually measure breaking under tension and shear they have no separate value, for the strength of a material not only depends on the mode of rupture but also on the way the stress is applied. For instance, a bending and a tensile test may be similar in that the material breaks under tension, but the results may differ very greatly, for under tension a large volume of material is subjected to the maximum stress while under bending the highly stressed portion is generally confined to a small part of the under surface opposite the point of loading. There are of course also other differences, and these will be discussed in a later section.

While it is important that all the differences involved in the different forms of static testing should be properly appreciated, it remains true to say that, for plastics, the results obtained show many more similarities than differences. There may be minor divergences, but generally, treatment of a given material leading to improvements in one form of static strength also leads to improvements in another. For this reason, and because of the larger amount of available information, the tensile test has been singled out for more thorough consideration in this chapter than the others.

Methods of Testing

While numerous minor variations in tensile testing exist the general principles remain similar. The procedure described here is taken from a standard specification for phenolic resins.[3] A dumbbell shape test specimen is moulded to the form and dimensions specified, and held in a testing machine between particular types of grip. The machine is set in motion so that the test piece is steadily extended and the minimum specified breaking load is reached in 1½ to 2½ min. The final breaking load is measured with an accuracy of at least 1 per cent, and from this figure the tensile strength may be calculated as a force per unit area using the original dimensions of the test piece. Precise conditions of moulding are also laid down to obtain reproducible results from a given moulding powder. Particular humidity conditions are not included in this specification, but they are of some importance wherever cellulose derivatives are involved, or indeed any plastic having an appreciable water absorption. For example, a humidity of 75 per cent has been prescribed for tests on synthetic resin bonded paper sheets.[4] Other types of tensile test have been devised by the A.S.T.M.[5]

The Conditions of Moulding

Any test measures only the properties of the test piece, so it is important for the test piece to be prepared in a consistent and, as far as possible, reproducible manner. However, even with the greatest care it is impossible to eliminate all variation in samples, though plastics generally give more reproducible results than glass. For example, a case has been quoted by Wainwright[6] where a standard deviation of 0.14 ft.-lb. was found in an impact test giving an average measurement of 5.0 ft.-lb. However, larger variations may sometimes be obtained.

Where differences occur in the conditions of moulding large variations in results may be obtained. For example, in an investigation carried out for the A.S.T.M.[7] it was found that variations in tensile strength between samples of ethyl cellulose moulded by different firms were as much as 35 per cent, and it was concluded that the temperature of moulding was a vital factor.

This conclusion is supported by the results of Ball *et al.*[8] who investigated the variation in the properties of injection moulded cellulose derivations, obtained by altering the injection cylinder temperature. They found that when this temperature was raised through 100° F. the tensile strengths of cellulose aceto-butyrate and ethyl cellulose mouldings were reduced about half, while impact strength and elongation at break *increased* by a factor of the order of two. When the rate of cooling of the plastic in the mould was altered there was no comparable change in the properties of the mouldings. With compression moulded polystyrene, however, different but somewhat more explicable changes took place under varying moulding conditions;[9] the strength properties, both in tension and impact, improved when the plastic had to travel a long way in the mould, and increased when the moulding temperature was lowered. These results can be explained by the orientation of the long chain molecules as the plastic material moves in the mould at a low temperature; this is supported by Muller[10] who deformed polystyrene at 100° C., 120° C. and 150° C. and found that the double refraction remaining in the cooled product was greater at the lower temperatures of deformation.

Theoretical and Real Tensile Strength

Actual values of the tensile strength or tenacity of plastic materials are mostly less than 1,000 kg./cm.^{2} ($\sim$ 14,000 lb./in.^{2}) and very much lower figures may be obtained. Apart from complex materials and orientated fibres, higher values are unusual. Theoretically this figure seems to be unexpectedly low, since a simple formulation of the structure of many plastic materials based on the known strengths of the valency bonds would lead to much greater tenacities. Numerous attempts have been made to relate real strengths to molecular structure; Mark[11] has summarized the results obtained from three models intended to represent the possible modes of rupture of orientated cellulose fibres. The strength of such fibres does exceed that of ordinary moulded and cast materials, but in some of these cases, where considerable elongation occurs under test, the strength, *calculated on the cross-section at the time rupture occurs*, may approach that of a fibre.

Mark calculates the tenacity of parallel orientated molecular chains with different rupture mechanisms.

(1) If the primary valency bonds of the chains are broken the tenacity should be 150,000 kg./cm.^{2}

(2) If the chains are arranged with all their ends in one cross-sectional plane and rupture occurs through Van der Waals' forces the tenacity should be 2,700 kg./cm.^{2}

(3) If the chains have a degree of polymerization of 400 glucose units and rupture occurs through the chains slipping over each other the tenacity should be 9,000 kg./cm.^{2}

On comparison with experimental results it is found that the strengths obtained with the best natural fibres, such as flax and hemp, are between the figures given by the second and third calculations, and Mark concludes that the third model most closely represents the results. Failure to reach the tenacities given by this calculation may be ascribed to the lack of ideal arrangements such as those considered in the model, i.e. to the presence of imperfections in the structure. However, Mark's fracture mechanisms (1) and (2) both involve the simultaneous fracture of a large number of molecular bonds, and the conclusion on structural irregularities would suggest that the molecular bonds are subject to a varying proportion of the applied stress. The possibility that some highly stressed primary valency bonds are broken in the fracture process is not, therefore, entirely excluded by these calculations.

Assumptions of structural irregularities or flaws appear to be more necessary where cross-linked phenolic plastics are concerned. Here it is difficult to visualize rupture without the breaking of strong primary valency bonds, since the whole structure is linked together by chemical linkages. For two typical phenolic type resins theoretical and experimental values of the tensile strength have been given by de Boer[12] and Houwink,[13] respectively (Table I).

TABLE I. THEORETICAL AND EXPERIMENTAL STRENGTHS OF TYPICAL CROSS-LINKED PLASTIC MATERIALS

Material	Theoretical strength for rupture of primary valencies	Theoretical strength for Van der Waals' forces	Experimental strength
	kg /cm ^{2}	kg /cm ^{2}	kg /cm ^{2}
Phenol formaldehyde resin ..	430,000	3,900	780
m-Cresol formaldehyde resin ..	380,000	3,200	380

Clearly the tensile strengths obtained in practice fall markedly below those predicted by theory. To account for this divergence Houwink suggests that the existence of flaws must be assumed, and that these are not to be taken as being accidental and due to exterior influence, but are rather structural features of a statistical nature. Though it cannot be said that the precise nature of such points of weakness is understood, this view is commonly accepted and it may be concluded that the tensile strength of many types of plastic material are reduced by some type of flaw, as is the case with glass. In other words tenacity is not a true bulk property in such materials.

However, there are certain consequences of this viewpoint which must apply to some extent to plastics, though the effects are much smaller than with glass. If tenacity is not a true bulk property, but is affected by the weakness of relatively rare parts of the material, then it will not be a uniform property throughout all large and small sections. So bending and tensile tests should not always give the same results even when the plastic bends in accurate accordance with the appropriate equations and breaks under tension; this conclusion is verified by the results of such tests which normally give higher results than pure tension, though this evidence may not be wholly significant.

Similarly variations with the size of the test piece are to be anticipated, but little work has been published on this topic apart from a recent paper by Lawton *et al.*,[14] in which it was found that the tensile strength of cellulose acetate and nitrate sheet increased notably as the thickness diminished. It is not clear whether these results furnish significant evidence for the existence of flaws which, according to the theories outlined, would be expected more particularly in plastics of the thermosetting type. The same effects could readily be caused by differences in molecular orientation.

Variation of Tensile Strength with Chain Length in Straight Chain Polymers

The third of the assumptions made by Mark for the theoretical calculation of tensile strength—that breakage occurs due to the slipping of molecular chains—leads naturally to a consideration of the interdependence of tenacity and chain length or degree of polymerization. Experiments have been carried out on moulded plastics, cast films, rubbers, and orientated fibres with generally similar results. If very low molecular weight materials are examined it is found that a certain minimum degree of polymerization is required before the material develops any measurable tenacity or is capable of being handled by conventional methods. Over this minimum size there is a rapid and roughly linear increase in tensile strength with molecular weight until a certain degree of polymerization is reached when increase of tensile strength falls off and subsequent increases in molecular weight lead only to slight improvements in tenacity. Curves of this type, taken from the work of Jones and Miles[15] on cast nitro-cellulose films are shown in Fig. 1; they are of great interest in that they also illustrate the considerable differences of tensile strength which result from casting the same polymeric material from different solvents. Similar curves showing the relation between tenacity and molecular weight have been given for methyl cellulose by Staudinger[16] and for ethyl cellulose by Ott.[17]

A thorough investigation of chain length-tenacity effects in fractionated polyvinyl chloride-acetate copolymers has been carried out by Douglas and Stoops.[18] A polydisperse solution of the original polymer in acetone was precipitated by addition of isopropanol, and six fractions of differing average molecular weights were separated. These materials were then moulded into suitable test pieces and their properties determined (Table II).

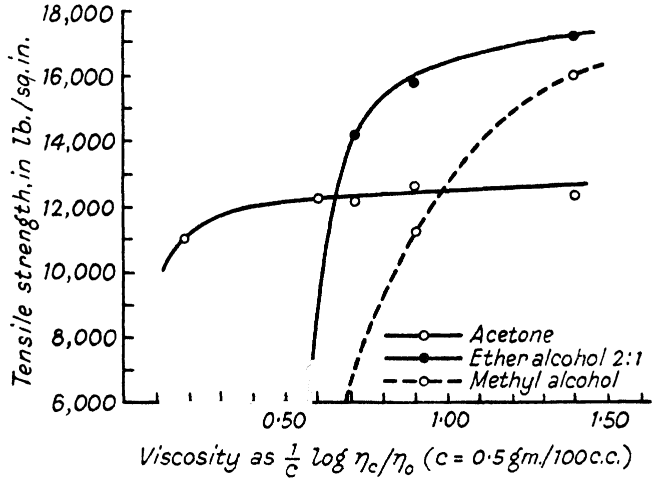

FIG. 1.—The tensile strength of cellulose nitrate film cast from various solvents plotted against the viscosity molecular weight.[15]

These results of Douglas and Stoops do not indicate very definite differences in behaviour between fractionated and unfractionated materials of the same average molecular weights, but, in the case of nitro-cellulose, this particular point has been examined under folding tests,[19] and the conclusion was reached that the presence of low molecular weight material in a mixture had an unfavourable effect. These and other results have been summarized by Mark[20] who considers, in agreement with his own experiments on cellulose acetate,[21] that the presence of 10 to 15 per cent of low molecular weight material has an unfavourable effect on strength properties in general.

TABLE II. THE VARIATION OF STRENGTH PROPERTIES OF VINYL CHLORIDE-ACETATE COPOLYMERS WITH MOLECULAR WEIGHT

Property	Original material	Fractionated sample					
		A	B	C	D	E	F
Molecular weight ..	10,600	15,800	14,600	13,200	11,100	7,500	5,800
Tensile strength, lb./in.²	9,025	9,955	9,745	9,630	9,180	6,680	1,120
Impact strength, ft.-lb.—piece ..	0·25	0·36	0·33	0·32	0·31	0·16	—
Modulus of elasticity, lb./in.²	400,000	418,000	407,000	401,000	403,000	394,000	350,000
Bending strength, lb./in.²	13,300	14,400	14,600	13,000	13,500	9,100	1,470

Sookne and Harris[22] examined the tensile strength of a number of cellulose acetate fractions and mixtures and concluded that this property in a mixture depends specifically on the number average molecular weight, but with a blend the actual value of the tensile strength was given by the weight average of the tensile strengths of the components. These apparently contradictory statements have been examined by Flory,[23] who showed that they could be reconciled only if the relation between molecular weight M and tensile strength f_T was of the form $f_T = a_0 + a_1/M$ (a_1 negative).

This relation is illustrated in Fig. 2, where tensile strength is plotted against $1/M$ from the results of Sookne and Harris. In another paper Flory[24] notes that this

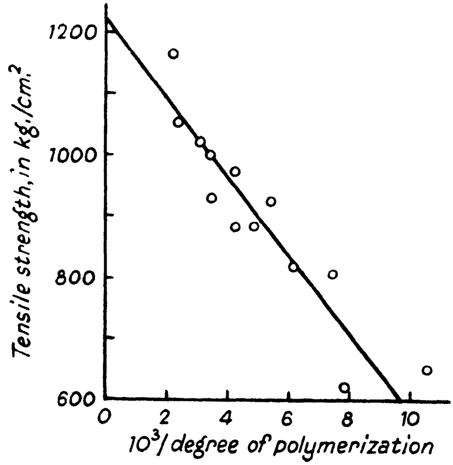

FIG. 2.—The tensile strength of cellulose acetate fractions plotted against the reciprocal of the molecular weight.[23]

result agrees with the views of Spurlin,[25] who considered that the failure of fibres under stress originated from the ends of the long chain molecules and should therefore depend on the number average molecular weight.*

In the same paper[24] Flory describes a fundamental and extensive

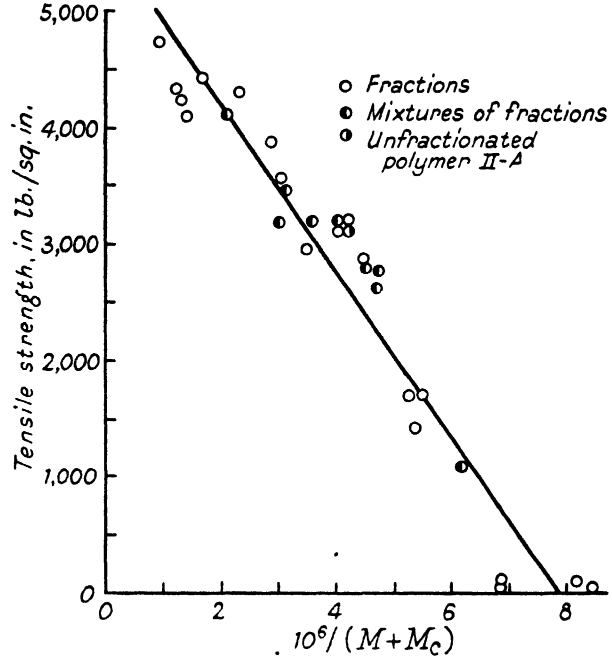

FIG. 3.—The tensile strength of a vulcanized butyl rubber in relation to the quantity $1/(M+M_c)$, where M is the molecular weight of the original polymer and M_c the molecular weight between cross links.[24]

investigation of the relation between mechanical properties, molecular weight and polymer structure in vulcanized butyl rubber; it was not possible to use a single quantity as a measure of the molecular weight, and Flory used the symbol M to describe the number average molecular weight of the original unvulcanized butyl rubber (which contained a small known amount of copolymerized isoprene for vulcanization), and M_c for the molecular weight of the vulcanized chains between points of cross linkage ($M > M_c$). In analysing the properties of the rubber two types of chain element had to be distinguished: (*a*) principal or "active" chains, each representing the portion of a molecular chain extending from one cross linkage to the next, and (*b*) terminal or "inactive" chains extending from the end of a primary molecule to the first cross linkage along its length. This distinction plays a vital part in Flory's theory since crystallization is considered as a fundamental process in the development of high tensile strength and only the active chains are assumed to be permanently oriented and crystallized during the stretching process. Flory shows that the proportion of material present as "inactive" or terminal chains is given by the relation $2M_c/(M + M_c)$, and demonstrates that the tensile strength of a rubber having a small amount of vulcanizable material present ($M_c = 37{,}000$) is approximately linear with $1/(M + M_c)$ (Fig. 3). He concludes that the tensile strength depends linearly on the fraction of "active" network present, capable of orientation.

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* The two main types of molecular weight measurement on a material containing a mixture of molecules having different molecular weights are defined as follows:

Number Average Molecular Weight $\frac{\Sigma M_i N_i}{\Sigma N_i}$

where N_i is the number of molecules of weight M_i.

Weight Average Molecular Weight $\frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i}$

The former is obtained from osmotic data and, in the case of straight chain molecules, the latter is given by viscometric measurements or light scattering.

Chain Structure and Tensile Strength

In the light of these theories it becomes of particular interest to consider the properties of other polymers where a non-linear chain structure such as is involved in branching or cross-linkage is known to occur. The importance of such differences in structure is shown in a paper by Whistler and Hilbert,[26] who studied the properties of amylopectin and amylose triacetates in film form. They found that the former gave a weak and friable product, but the latter gave good films of excellent strength. This large difference in behaviour was not to be explained by differences in molecular weight since the films derived from amylopectin were made from a material well above the minimum molecular weight for film formation, but were explained by the fact that the amylopectin has a branched chain structure while the amylose is a straight chain polymer. This would agree with the theory of Spurlin,[25] applicable to cellulose derivatives, as the existence of a number of side chains would increase the number of chain endings for any given molecular weight. It is therefore clear that structural factors as well as molecular weight play an important part in determining the strength of polymeric materials. Rather less work has been published on the effect of cross-linking agents on the strength of ordinary synthetic thermoplastics. Some experiments carried out by the author showed that glycol dimethacrylate polymerized by itself to give a weak friable solid, similar to a silica gel; but it could be copolymerized with methyl methacrylate and varying quantities of plasticizer to give flexible films which did not dissolve in acetone, although swelling occurred when only small quantities of the glycol dimethacrylate were used. However, such films showed no noticeable improvement in strength, and when 1·5 per cent or more of the cross-linking agent was used they became increasingly brittle; on the other hand Trevy,[27] working with vinyl chloride-acetate copolymers, has reported that small improvements in strength can be obtained by copolymerization with such materials as allyl crotonate or glycol dicrotonate. Similarly, with polystyrene Goggin and Boyer[28] report that a maximum in the tensile and impact strengths is found when 5 per cent divinyl benzene is incorporated as a cross-linking agent. The favourable effects obtained in the vulcanization of rubber are also well known. The only possible conclusion is, therefore, that the effect of cross-linking agents with thermoplastic materials is not a general one but depends on the polymer and the mode of action of the cross-linking agent.

Recently some cross-linked polymeric materials have been developed with useful mechanical properties. They are prepared by the polymerization of the diesters of allyl alcohol (e.g. di-allyl phthlate) and other compounds having two polymerizable groups. In general it appears that the molecular weight of the original monomer from which they are formed is fairly large—over 200—and that this helps to reduce the shrinkage during polymerization and so facilitates their technical application. It may also be a factor in the development of good mechanical properties in materials formed by this type of cross-linking action.

Effect of Temperature on the Tensile Strength of Thermoplastic Materials

It is to be expected that the tensile strength of a thermoplastic will vary with temperature. In general, the amount of the variation is considerable, and with nearly all thermoplastics a rise within the normal temperature range causes a *decrease* in tensile strength. One exception is provided by polyvinyl chloride,[29] which shows a maximum tensile strength at about 0° C., but the usual decline with temperature has been recorded by Carswell and Nason,[29] Haward,[30] and Kistler[31] for ethyl cellulose, cellulose acetate and acetate butyrate, methyl methacrylate, polystyrene, and various vinyl polymers. Some results given by Carswell and Nason[29] (Fig. 4) show the anomalous behaviour of polyvinyl chloride, and also

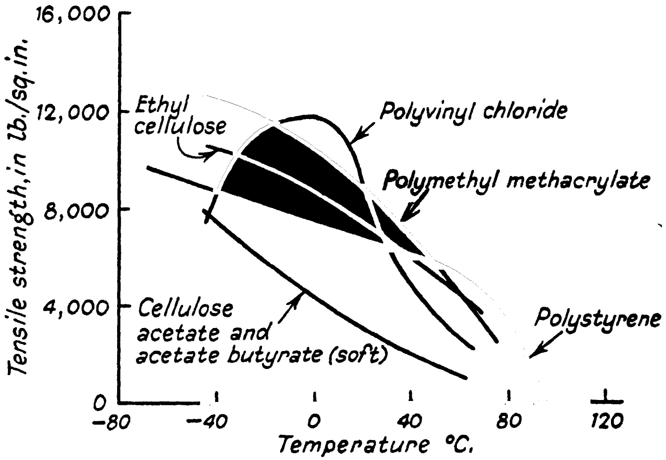

FIG. 4.—The temperature variation in tensile strength for thermoplastics.[29]

the considerable differences observed among those thermoplastics whose tensile strength does decline as the temperature rises; a material may be stronger than another at one temperature, but the position may be reversed at a different temperature.

Some more extensive experiments have been carried out on fibres by Busse *et al.*,[32] whose results were also strongly dependent on the time taken for testing. They concluded that temperature and fatigue effects were dependent on plastic and viscous flow within the fibres, and interpreted their results on the assumption that an energy of activation was involved. They plotted the relation

$$\log(\text{breaking time}) = E/RT + B$$

at a particular stress and obtained good linear relations for log (time) against 1/temperature. From these they calculated the following activation energies of the flow process concerned in the breaking of different fibres.

Rayon	8,000 cal./° C.
Cotton	12,500 cal./° C.
Nylon	20,000 cal./° C.

The same treatment may be applied to the curves shown in Fig. 13, which are primarily intended to illustrate the time factor. By drawing a series of vertical lines at four different stresses, four separate groups of results may be obtained and treated according to the above relation to give a stress-independent energy of activation of 14–15,000 cal./° C. This result would appear to support the extension of Busse's treatment to plastics as well as fibres.

Outside the normal temperature range there is not very much evidence concerning the tensile strength of thermoplastic materials, but some figures quoted by Melville[33] show that the strength of cellulose compounds is *reduced* at − 195° C., and some figures by Röhm[34] for methacrylate show a tensile strength reduced from 750 kg./cm.^{2} at − 20° C. to 680 kg./cm.^{2} at − 40° C. If this reversal of trend proves to be general for thermoplastics, there will clearly be a temperature region where the theory of activation outlined does not apply and the behaviour of thermoplastics will have to be regarded as essentially similar to that of the thermosetting resins.

Effect of Temperature on the Tensile Strength of Thermosetting Resins

The thermosetting resins, which have a three dimensional structure, are not affected in the same uniform manner by temperature changes in the range 0 to 100° C. as the thermoplastic materials. Some typical examples have been given by Kistler[31] (Fig. 5). They agree with the results of Carswell *et al.*[35] (Figs. 6, 7, 8 and 9), though differences are found in the case of complex filled materials. At low temperatures these resins are relatively weak; their tensile strength increases up to a certain limit and then decreases again as the temperature is still further raised. Clearly this cannot be accounted for by a single activation mechanism, and Kistler has suggested the material is weak at low temperatures because of the difficulty of distributing the stress throughout the test piece. At higher temperatures a greater deformation occurs and pockets of high stress concentration are relieved. In higher temperature ranges the decline in tensile strength resembles that of

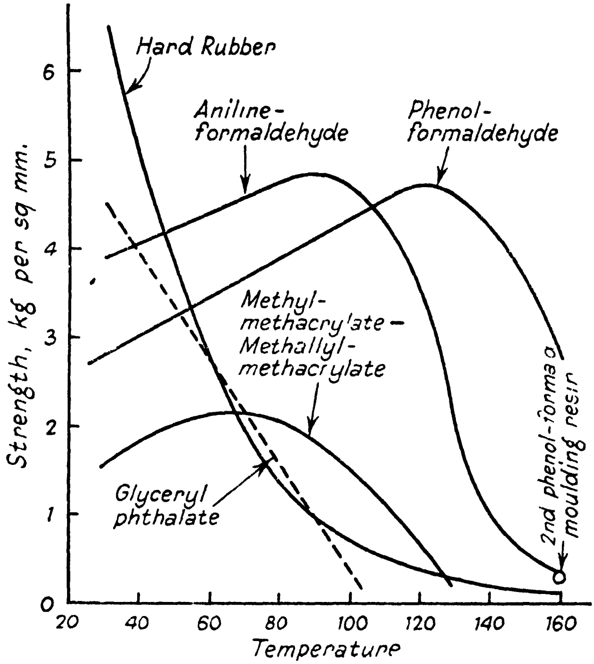

FIG. 5.—The tensile strength of cross-linked plastics against temperature. The typical thermosetting materials show a maximum [31]

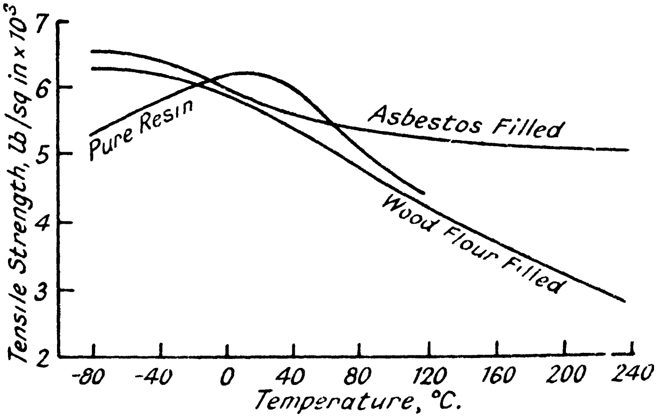

FIG. 6—The temperature variation of the tensile strength for a phenolic resin. The pure resin shows a maximum.[35]

thermoplastic resins, and it is concluded that intermolecular forces of a secondary character are involved. As far as the primary valencies are concerned the mode of rupture must bring great

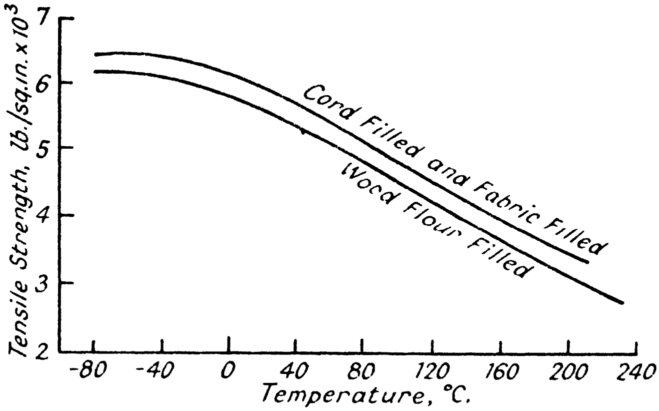

FIG. 7.—The temperature variation of tensile strength for a reinforced phenolic resin.[15]

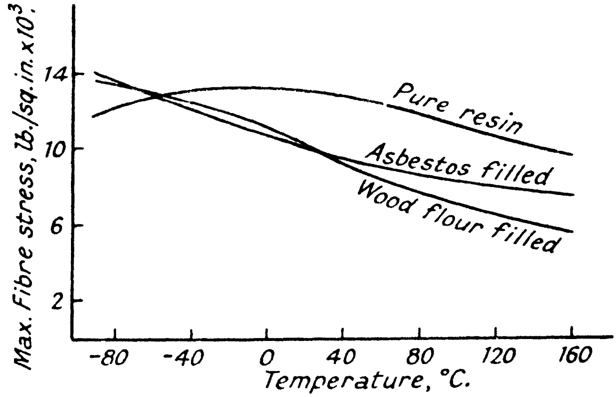

FIG. 8.—The temperature variation of the bending strength (max. fibre stress) for a phenolic resin. The pure resin shows a maximum.[15]

stresses to bear on a few valency bonds and prevent them from redistributing the load. This appears to be an alternative formulation of Houwink's[13] theory of flaws. Nevertheless, the fact that the decline in strength does not occur over the whole normal temperature range with the thermosetting resins, together with the possibility of compounding them with less temperature sensitive fillers (e.g. glass) makes them the most suitable plastic materials

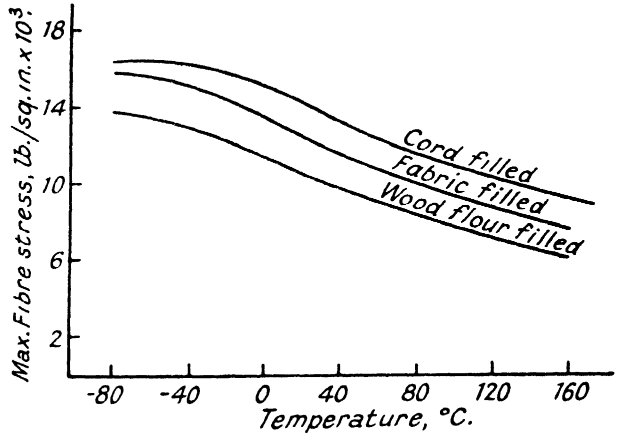

FIG. 9.—The temperature variation of bending strength (max. fibre stress) for a reinforced phenolic resin.[35]

where high static strength is required over a fairly wide range of temperature.

Effect of Plasticizers and Substituent Groups

Numerous experiments have been recorded on the effect of plasticizers on the tenacity of different plastics and the general character of the phenomena is not in doubt. Addition of plasticizer softens the resin and leads to a decrease in tensile strength. However, the harmful effect of this decrease is generally more than compensated in use by improvements in flexibility and impact strength. Thus addition of plasticizer has a similar effect to an increase in temperature.

Typical information may be obtained from papers by Gloor,[36] Kirkpatrick[37] and Fordyce and Meyer.[38] A few typical figures for cellulose acetate and acetate butyrate taken from the last paper are given in Table III.

These figures also illustrate a fresh but related property. If the same quantity of plasticizer is used for cellulose acetate and acetate butyrate films a softer material of low tensile strength will be obtained with the acetate butyrate. Thus the latter requires less plasticizer than cellulose acetate owing to the plasticizing action

TABLE III. EFFECT OF SOME PLASTICIZERS ON THE MECHANICAL PROPERTIES OF CELLULOSE ACETATE AND ACETATE BUTYRATE

	Dimethyl Phthalate						Diethyl phthalate					
	Cellulose acetate			Cellulose acetate butyrate			Cellulose acetate			Cellulose acetate butyrate		
Parts plasticizer per 100 parts base	37·8	30·0	22·6	15·8	11·0	6·3	59·5	49·0	38·7	17·0	12·0	7·0
Flow temperature, ° F.	266	285	307	266	285	307	266	285	307	266	285	307
Per cent elongation . .	8·0	6·5	5·0	23·8	22·7	21 8	40·0	28·6	20·8	26·2	24·7	23·4
Tensile strength, lb./in.^2	6,630	8,100	9,930	4,690	5,520	6.540	2,860	3,850	5,100	4,410	5,340	6,470
Flexural strength, lb./in.^2	11,140	14,200	17,000	7,840	9,240	10,950	3,930	6,050	8,800	7,390	8,920	10,800
Rockwell hardness, *M* . .	79·5	90·5	101·1	72·4	80·1	86·4	49·0	59·7	75·5	65·5	75·2	84·3

of the butyl group—a property which is of value for weathering stability. A similar softening effect is observable in the series of polymers obtained from methyl, ethyl, and butyl methacrylates; the figures quoted in Table IV are taken from a paper by Dittmar and Strain,[39] which also showed that the *n*-butyl is softer and of lower tenacity than the isobutyl methacrylate.

TABLE IV. MECHANICAL PROPERTIES OF THREE POLYMERIZED METHACRYLATES

	Methyl	Ethyl	Butyl
Hardness number	220	141	1
Tensile strength, lb./in.^{2}	9,000	5,000	1,500
Impact strength, kg./cm.^{2}	10·5	7·1	11·5
Extension at break, %	4	7	230

Similar results for the tensile strength of cellulose tri-esters have been given by Sheppard and Newsome[40] (Fig. 10). An explanation has been put forward by Coumolous and Crisp[41] in the course of a discussion on a paper by Tuckett.[42] Short hydrocarbon groups are considered to extend on each side of the main molecular chain and so, to reduce the interaction between them, a conclusion which was supported by certain experiments on the force area relationship of unimolecular films. Thus flexible hydrocarbon side chains can act as an internal plasticizer.

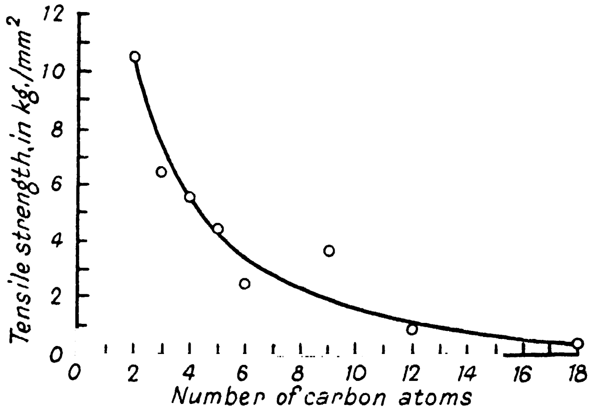

FIG. 10.—The tensile strength of the cellulose esters obtained from normal carboxylic acids having different numbers of carbon atoms.[40]

With the ordinary types of plasticizers used with plastic materials the question arises: how much of any given plasticizer must be added to produce a specified effect on the mechanical properties? At present no adequate and accepted theory of plasticizer action exists, but one point has been emphasized by Jones.[43] He has shown that in the case of polyvinyl formals the tensile strength of compositions containing equal parts of plastic and plasticizer gives a smooth curve when the results for different plasticizers are plotted against plasticizer viscosity. A similar correlation is shown by some Hycar synthetic rubber compositions. Jones also shows that, with plasticized polyvinyl chloride-acetate, a similar correlation exists between deformation properties and plasticizer viscosity. Such observations are a useful approach to an obscure problem.

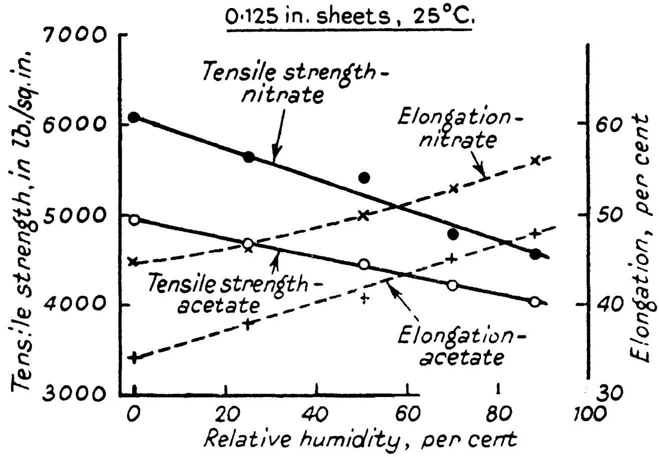

FIG. 11.—The effect of varying humidity on the mechanical properties of cellulose ester sheeting.[14]

Besides specific plasticizers introduced to influence its properties, the tensile and other strength characteristics of a plastic may also be affected by the presence of varying amounts of residual solvents, or water vapour absorbed from the atmosphere. The importance of controlling humidity in strength tests may be illustrated by quoting results[14] with cellulose acetate and nitrate sheet (Figs. 11 and 12). It will be seen that both materials absorb water from the atmosphere in quantities that increase markedly above 50 per cent humidity and at the same time the tensile strengths are steadily reduced. The general effect is similar to that of increasing the plasticizer content and also generally leads to a decrease in the

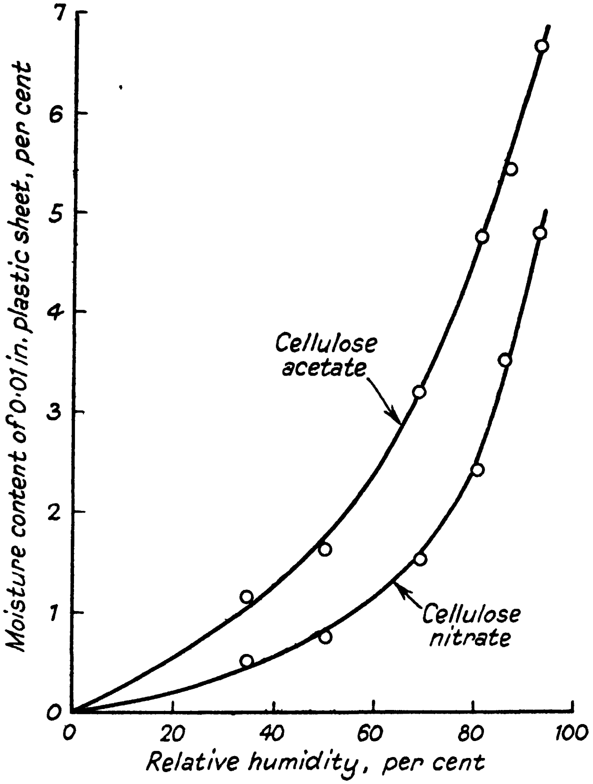

FIG. 12.—The relation between relative humidity and moisture content for cellulose ester sheeting.[14]

stresses required to produce a particular deformation and an increase in the impact strength with cellulose derivatives.

The Time Factor

It is characteristic of plastic materials that when any static strength measurement is made the results obtained depend very much on the time allowed for fracture to take place. In some ways this behaviour is analogous to the problem of fatigue in metals, though, as pointed out by Bartoe and Frederick,[44] there is a distinct difference in the characteristic properties of the two groups of materials. With metals the most damaging effects are observed as the result of vibrations and alternating stresses, whereas with plastics the steady application of small loads is likely to have the more serious consequences. Naturally plastics are also affected by alternating stresses, but their behaviour under these conditions is not as straightforward as metals'. For example, Lazan[45] has shown that under oscillating stresses the work absorbed by a plastic material may bring about a temperature rise of 40° C. or more, and for this reason such results can only be properly assessed when temperature strength variations are also known. Also, since temperature changes will entail variation in the elastic constants experiments based on applying a repeated deformation to a plastic may lead to ambiguous results, largely dependent on cooling conditions of the test piece. Where resistance to alternating stress systems is vital it would therefore be advisable to base tests as far as possible on the actual parts and modes of operation likely in use; this property of converting kinetic into thermal energy is in many respects a useful one.

With regard to the behaviour of plastics under a steady stress reference has already been made to the tensile strength of plastics being *time-sensitive*, and that in specifications definite rates of application of stress are laid down. No doubt comparison of specific results on this basis is satisfactory for many purposes, but the subject of time effects deserves more attention both in theory and practice. Firstly, any investigation of the effect of different variables on the strength of plastics should preferably be carried out at a series of times so that the conclusions reached are not themselves time-sensitive. For instance, if the short-time strength of plastics eventually proves to be much larger than that obtained by experiments made at the normally specified rates, then this property must be considered in the relation of theoretical and experimental tenacity. Secondly, tensile tests for use made at a standardized rate will only give a true comparison of the value of the two plastics if the degree of time sensitivity of the two materials is the same or if the times involved in use and testing are similar.

Investigations of the time factor have been carried out on *thermoplastic* materials by Findley,[46] Couzens and Wearmouth,[47] and Haward.[30, 48] In experiments covering polyvinyl chloride, cellulose nitrate and plasticized cellulose acetate, all these workers agree that their materials have a limiting upper value of tensile strength at which they tend to break at short times of rupture. This property is illustrated in log. breaking time curves (Fig. 13). In such cases it is clear that at least one tensile stress, namely: the extrapolated short time breaking stress, exists which is essentially time independent and to which theory can be directed in the absence of a full understanding of the breaking time curve. However, the theory of these curves has hardly yet begun to be developed. The work of Busse *et al.* already quoted relates breaking time and temperature but makes no reference to stress. A semi-empirical explanation of such a stress-time curve was put forward by Haward, on the assumption that the process of rupture was a continuous one in which the short-time strength of the material was gradually reduced under the operation of the stress. His

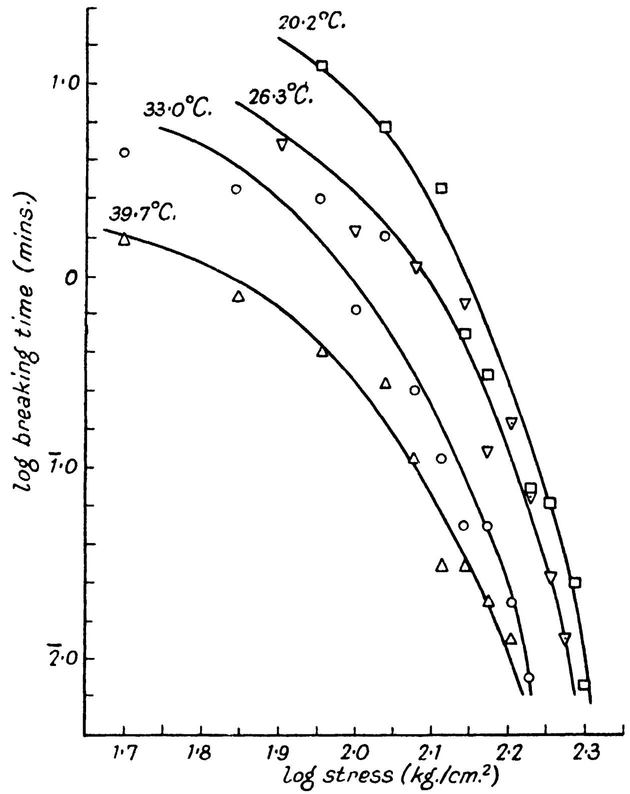

FIG. 13.—Logarithmic curves showing the fracture of plasticized cellulose acetate film under constant load.[30]

cellulose acetate whitened at slow breaking times, in line with the theory and suggesting that small holes may be torn in the material as it breaks. A feature of these cellulose acetate films, and also of those investigated by Findley,[46] was that the deformation at break in times of the order of a minute was greater than that obtained when the material was broken in periods of an hour, but Lawton *et al.*,[14] also working with cellulose acetate, obtained contrary results. So it is obvious that few generalizations can be made. Although much published work agrees on the tendency to a definite breaking stress at short-times with a number of thermoplastics, some unpublished experiments by the author on cellulose acetate butyrate have yielded no evidence of such a limiting stress down to breaking times of a few seconds, and nor does the work of Lawton *et al.*[14] covering a limited time ratio of 100 : 1.

In *thermosetting* materials there is little doubt that time-sensivity also occurs. Experiments, mostly with laminates, have been reported by Chasman,[49] and Gailus and Telfair,[50] who find that the stresses necessary to cause rupture in 1,000 hr. are 67 per cent or less of those occurring in the ordinary A.S.T.M. tensile test. No evidence suggesting the existence of an upper limit of tenacity at short times was obtained.

The time-sensitivity of a material has an important influence on the degree to which its properties are dependent on its previous history. In at least one case, previous treatment yielded very drastic results.[48] A piece of cellulose acetate was subjected to a load under which it normally extended and broke during a period of 7 minutes. Other pieces were then subjected to the same load under the same conditions for shorter periods, when they suffered deformation without fracture. These pieces were then warmed at 60 to 70° C. for 10 minutes when their deformation disappeared. They were then again subjected to the same load. This time they broke in a shorter time, such that the sum of the two loading times came to about 7 minutes. These results show that the damage done by a stress may not be removed when the deformation caused at the same time by the same stress is eliminated. It also seems that in this case rupture and deformation were two independent processes.

Bending Strength

When a long beam of a rigid isotropic material, which obeys Hooke's law, is simply supported at each end and broken under a centrally applied load, normal to the surface of the beam, the highest tensile stress in the material is underneath the beam, opposite the point of application of the load, and is given by the relation:

$$\text{Bending strength} = f_B = \frac{3Pl}{2bh^2}$$

where l,b,h are the length, breadth and thickness of the beam and P is the load required for fracture. This quantity f_B is variously known as the bending strength, flexural strength, or modulus of rupture of the beam. The bending strength is a stress, and is in principle the same as the tensile strength, though in actual tests different and usually higher figures are obtained. The difference may be ascribed to the following causes:

(1) The beam is not a long beam as assumed in the simple theory of bending.

(2) The deflection of the beam at fracture is larger than the theory assumes.

(3) The material of which the beam is made does not obey Hooke's law.

(4) The volume of material subject to the maximum stress is smaller in a bending than in a tensile test.

The first three all have one point in common, namely: *the stress deduced from the above formula does not correspond with that actually present in the material when fracture takes place.* On the other hand the last factor represents a *genuine* property of the material which may give rise to a variation between bending and tensile tests even when the simple bending relations are strictly obeyed.

The divergence of the *first* factor from the simple theory arises from the fact that the beam is not long in comparison with its thickness, and from the effect of shearing forces not considered in the simple bending treatment. In general, it seems that the effect of these shearing forces is small when the span-depth (length-thickness) ratio is greater than 10 : 1. For instance, Zinzov[51] has suggested that beams may be regarded as long when the span depth ratio is above 8 : 1, while Timoshenko[52] presents two methods of allowing for the shearing forces in calculating the deflection of beams under central load and finds that this deformation will be increased by the factors $(1 + 3{\cdot}9\, h^2/l^2)$ and $(1 + 2{\cdot}85\, h^2/l^2 - 0{\cdot}84\, h^3/l^3)$ in each case. Thus the expected departure of the deformation from that predicted by the simple formulae are less than 4 per cent when h/l is less than 1/10. Finally, whenever the deformation of a beam is used as a method of measuring the elastic constants of the material allowance must be made for deformation at the point of loading; but this is not so important in connection with the calculation of the maximum bending stresses which are on the opposite side of the beam.

A quite different source of error can arise when the beam is of the opposite sort, i.e. particularly long and thin. In this case, there is a tendency for the beam to give large deflection (*second* factor), so that it cannot be regarded as rigid and gives a deformation which is large compared with the thickness and even comparable with the length. The theory of stresses and deformations here has been considered by Freeman.[53] His results show that for a material obeying Hooke's law the departures from the simple theory of bending are more serious as regards the deformation of the beam than the bending stresses. For example, where the ratio of the deformation obtained over the length is 0·24 the error expected in using the simple theory to calculate the deformation is 14 per cent, whereas that in the calculation of the bending strength is 0·6 per cent. Thus it may be assumed that large deflections in simply supported beams are not likely to cause serious errors in the calculation of bending stresses, except in combination with other sources of error.

The *third* factor, that of the material not obeying Hooke's law, is undoubtedly of the greatest importance, especially with thermoplastic materials as these are characteristically capable of large deformations not even approximately proportional to the applied stress. With some of these plastics the effect is that a small increase of the stress in the range of stresses required for fracture can lead to a large increase in the amount of the deformation. Under such conditions it is likely that large deformations in the most highly stressed portions of the beam will lead to the distribution of the tensile forces over a much larger area of the material than assumed in the simple theory, and therefore to high values of the calculated bending strength.

Finally remains the *fourth* factor, the question of the volume of material subject to a high stress. Any material in which the stress required for fracture is determined by the existence of flaws or heterogeneities, is also likely to be size-sensitive with regard to its fracture stresses. This problem is very important in con-

nection with the behaviour of glass, concrete, and cast iron, but theories have also been put forward suggesting that the strength of plastics, especially the thermosetting type,[13] is also dependent on the existence of flaws. Should such theories prove correct they will also throw light on the problem of bending strength.

In view of the many factors involved it is hardly to be expected that the results obtained from bending tests will be the same as those found in tension. Indeed the various doubts and errors involved are held by de Bruyne[54] to be so large that he considered the results of bending strength measurements had little meaning with plastics. Nevertheless since actual materials are frequently broken in flexure under service conditions the practical worker needs to utilize some bending tests even when the results are only of minor theoretical interest. It is therefore important to note that results of all the three major factors influencing the results of bending tests (factors 1, 3 and 4) are such as to cause the bending strength as normally calculated to be above the tensile strength. Typical examples of such normal behaviour are included in Tables II and III, but such figures throw no light on the source of the differences obtained.

More systematic investigations of this problem have been carried out by Zinzow[51] and by Schoenborn, Proctor and Carvajal.[55] Experiments were made in which the length of the beam was varied to give differing span-depth ratios using a beam of constant depth, and it was found that the calculated flexural strength normally decreases with increasing length. Since the range of span-depth ratios covered in these experiments was mostly below 10 : 1 the effects were correlated with the first of the factors mentioned, namely: the effect of the beam having an appreciable depth.[51] With regard to the deformation of these beams it was found that the apparent modulus of elasticity (after correction for indentation when necessary[51]) increased as the span-depth ratio was raised; as predicted by Timoshenko[52] shorter beams deformed more easily than the simple bending relations predicted. This behaviour occurred even when the elastic modulus of polystyrene was calculated for *small* deformations and did not therefore seem to be connected with departures from Hooke's law; thus there seems no reason to doubt that the use of short beams in a bending test does lead to results which are appreciably affected by the action of shearing forces.

Naturally these investigations on the effect of the span-depth ratio do not throw much light on the other two factors which may be expected to influence the results of a bending test. These other factors do not seem to have been the subject of much experimental work, but some results obtained by Burns and Werring[56] in which the bending strength of a cellulose acetate plastic increased as the temperature was raised from 23 to 49° C. point to the action of the third factor, namely: departure from Hooke's law in deformation. Cellulose acetate is a plastic known to be capable of large non-ideal elastic deformations which are more easily developed at higher temperatures. On the other hand an actual increase in the stress required to fracture this material seems most unlikely in the temperature range of the tests. The results can therefore be interpreted as due to a greater redistribution of the stress at higher temperatures.

It is important to realize that a general parallelism does exist in many cases between the various sorts of static strength measurement (Figs. 6, 7, 8 and 9). The behaviour is qualitatively similar; for instance the pure phenolic resin gives a maximum in the same temperature range both in bending and tension, and the two filled materials show a steady fall in strength with temperature in each case. On the other hand the effects are not the same quantitatively, the effect of temperature changes being less drastic on bending strength than on tenacity. Such results may be looked upon as characteristic of the harder types of plastic material to which the bending test is most frequently applied. Where a plastic is of the soft and flexible type no sensible measurement can be made on the lines of the ordinary bending test discussed above.

Shearing Strength

The fracture of a plastic material may occur in more than one way. In particular, the process can be envisaged either as a separation of the material along lines of tension, or as a movement of parallel planes under the action of shearing forces. Actually it is not easy to be certain of the precise mode of fracture in any given test, since both tensile and shearing stresses are generally present. In some bending tests fracture may take place under shearing forces, as when the separation of planes in a laminated material is observed. It is therefore the object of testing procedure to devise tests in which either the tensile or shearing forces will be the larger. A test is given in B.S. 1137: 1943 of shearing forces for synthetic bonded paper sheets. Other methods have been devised by the A.S.T.M.[57]

B.S.I. Method of Test

The apparatus used in the test consists of a circular punch and die (Fig. 14). The punch is to be a running fit in the die. The dimensions of the specimen shall be 3 × ¾ in. and of any thickness up to ½ in. In carrying out the test the load is increased so as to reach the specified shearing stress in approximately 2 min. and the shear is calculated from the formula

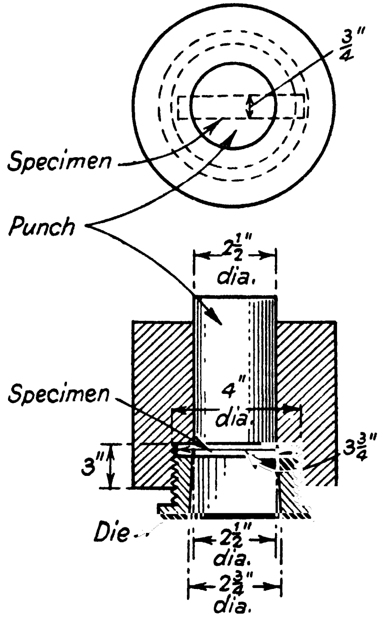

FIG. 14.—The apparatus used for the B.S.I. method for testing the shear strength of plastics.

$$f_s = \frac{P}{2\,b\,h\,K}$$

f_s = Shear stress in lb./in.^{2}
P = Shearing load in lb.
b = Width of specimen in in.
h = Thickness of specimen in in.
K = 1·016 to allow for curvature of sheared surface.

As stated above shear strength has not been measured as frequently as tenacity. With phenolic materials the work of Cox and Pepper[58] indicates that, whereas the shear and tensile strengths of an unreinforced phenolic resin are about the same, when a paper filler is used the tensile strength alone is greatly increased. Using cellulose derivatives Lawton *et al.*[14] obtained generally lower values in shear than in tension, especially at low temperatures.

Compressive Strength

The compressive strength of a material represents the one dimensional compressive stress which it can stand for a specified time without rupture. Methods of measurement include the compression of a 1 in. cube (B.S. 1137: 1943) or a right cylinder 12 mm. long × 12 mm. diameter (B.S. 903: 1940 for vulcanized rubber) for 1 min. Both these specifications also stipulate that the material must not yield more than a definite amount, and in this respect they test deformation as well as static strength. As far as rupture is concerned, breakdown may occur by delamination in the case of laminated materials or by the action of shearing forces at 45° as noted by Barron.[59] Where this occurs the measured compressive strength should be equal to half the true shear strength of the material, since any compressive force may be resolved into shearing forces of half its magnitude acting at 45°. An example of failure under shear in a compression test is given on Plate XII.

TABLE V

Material	Compression strength	Shear strength	Ratio
	f_c lb /in ^{2}	f_s lb /in ^{2}	f_c/f_s
Batch No. 202414	13,306	6,504	2·04
Batch No. 173414	14,810	7,739	1·92
Batch No. 172412-3	14,896	7,436	2·00
Batch No. 252411	11,200	6,469	1·67
Batch No. 202412	6,720	3,495	1·93

A similar type of behaviour is common with metals, where it has, however, been found that the line of slip is not always at 45° to the direction of the compressive forces, but differs by an angle of $\phi/2$ where $\tan\phi = \mu$ the coefficient of sliding friction.[60] In such cases the shearing stress under which fracture occurs will not be half the compressive stress and the compressive strength will be given by the relation

$$\text{Compressive strength} = f_C = 2f_S \tan\,(45 + \phi/2)$$

Thus in general the compressive strength of a material is only equal to twice the shear strength when these frictional effects are small. However, since not much is known about these frictional forces with plastics it is of interest in the first place to compare shear and compression tests to see whether a 2 : 1 relation is followed. Direct comparisons of shear and compressive strengths may be made on the basis of test results supplied by Messrs. Catalin Ltd., and carried out by the Sheffield Testing Works on cast phenolic resins. The form of the break under compression was that of vertical splitting, which did not of itself suggest shear. On the other hand the quantitative relations between the results was satisfactory (Table V).

Figures showing agreement in the case of similar unfilled resins are also given by Smith,[61] though he gives other figures for filled materials in which shear and compression do not appear to be simply related.

Effect of Exposure to Atmospheric Conditions

It may be noted here that the static and also other strength properties of plastic materials are, in general, liable to deteriorate on exposure to atmospheric conditions. These effects have been investigated by Lawton and Nason[62] on certain cellulose derivatives where they are particularly severe. They showed that the changes were more drastic in a sub-tropical than in a temperate climate, but even in the latter the tensile strength of cellulose nitrate sheet declined from 6,000 to 1,500 lb./in.^{2} in 6 months' exposure, and cellulose acetate showed a reduction from 5,500 to 5,000 lb./in.^{2} in 12 months. Other strength properties showed a parallel decline, except the modulus of elasticity which showed a slight increase with the nitrate and a considerable increase with the acetate, probably due to the leaching out of the plasticizers. This was one important aspect of the weathering process. Substantial degradation of the cellulose molecule also occurred, notably with the nitrate, and this effect was more drastic in the surface layers than in the bulk of the sheet. Other changes included shrinkage, ester hydrolysis, and the release of delayed elastic deformations frozen in the material at the time of its manufacture.

REFERENCES—II

(1) Treloar, L. R. G.: *Reports on Prog. of Physics*, **9** (1943), p. 113.
(2) Weibull, W.: *Ingeniörsvetenskapakadamiens Handl.* (1938), p. 149.
(3) B.S.S. 771 (1938): *Mouldings and Moulding Materials.*
(4) B.S.S. 1137 (1943): *Synthetic Resin Bonded Paper Sheets.*
(5) *A.S.T.M.*: D 638–44 T; D 651–42 T.
(6) Wainwright, C.: *Brit. Plast.*, **18** (1946), p. 524.
(7) *A.S.T.M.*: Bull. **140** (May 1946), p. 45.

(8) BALL, R. H., LEYES, C. E., MELNYCHUCK, A. A.: *Ind. Eng. Chem.*, **37** (1945), p. 240.

(9) AMOS, J. S.: *Colloid Chemistry*, ed. Alexander, Vol. VI, pp. 992–1009 (Reinhold Publishing Co., 1946).

(10) MULLER: *Angew. Chemie*, **63** (1940), p. 425.

(11) MARK, H.: *Cellulose and its Derivatives*, ed. E. Ott, p. 1001 (Interscience Publishers Inc., New York, 1943.)

(12) DE BOER, J. H.: *The Phenomena of Polymerisation and Condensation* (Faraday Soc. Discussion, 1935), p. 28.

(13) HOUWINK, R.: (Faraday Soc. Discussion, 1935), p. 128.

(14) CARSWELL, T. S., LAWTON, T. S., NASON, H. K.: *Mod. Plast.* (Oct. 1944), p. 145.

(15) JONES, G. G., MILES, F. D.: *J. Soc. Chem. Ind.*, **52** (1933), 251 T.

(16) STAUDINGER, H.: *Papier Fabrikat*, **48** (1938), pp. 377, 381, 473, 481.

(17) OTT, E.: *Ind. Eng. Chem.*, **32** (1940), p. 1641.

(18) DOUGLAS, S. D., STOOPS, W. N.: *Ind. Eng. Chem.*, **28** (1936), p. 1152.

(19) SPURLIN, H. M.: *Ind. Eng. Chem.*, **30** (1938), p. 538.

(20) MARK, H.: *Cellulose and its Derivatives*, *ibid.*, p. 1009.

(21) MARK, H.: *Paper Trade Journal* (July 1941), p. 34.

(22) HARRIS, M., SOOKNE, A. M.: *Ind. Eng. Chem.*, **37** (1945), p. 478.

(23) FLORY, P. J.: *J. Am. Chem. Soc.*, **67** (1945), p. 2048.

(24) FLORY, P. J.: *Ind. Eng. Chem.*, **38** (1946), p. 417.

(25) SPURLIN, H. M.: *Cellulose and Cellulose Derivatives*, ed. E. Ott, pp. 935–7 (Interscience Publishers Inc., New York, 1943).

(26) WHISTLER, D. L., HILBERT, G. E.: *Ind. Eng. Chem.*, **36** (1944), p. 296.

(27) TRÉVY, P.: *Rév. Gén. Mat. Plast.*, **13** (1937), p. 147.

(28) BOYER, R. F., GOGGIN, W. C.: *Ind. Eng. Chem.*, **38** (1946), p. 1090.

(29) CARSWELL, T. S., NASON, H. K.: *Mod. Plast.* (June 1944), p. 121.

(30) HAWARD, R. N.: *Trans. Farad. Soc.*, **39** (1943), p. 267.

(31) KISTLER, S. S.: *J. App. Phys.*, **11** (1940), p. 769.

(32) BUSSE, W. F., LESSIG, E. T., LOUGHBOROUGH, D. L., LARRICK, L.: *J. App. Phys.*, **13** (1942), p. 715.

(33) MELVILLE, H. W.: *Reports on Prog. of Physics*, **5** (1938), p. 64.

(34) RÖHM, O.: *Chem. Fab.*, **9** (1936), p. 360.

(35) CARSWELL, T. S., HASLANGER, R. U., TELFAIR, D.: *Mod. Plast.* (July 1942), p. 65.

(36) GLOOR, W. F.: *J. App. Phys.*, **12** (1941), p. 420.

(37) KIRKPATRICK, A.: *J. App. Phys.*, **11** (1940), p. 225.

(38) FORDYCE, C. R., MEYER, L. W. A.: *Ind. Eng. Chem.*, **32** (1940), p. 1053.

(39) DITTMAR, H. R., STRAIN, D. E.: *Trans. Amer. Electro. Chem. Soc.*, **74** (1938), p. 181.

(40) Sheppard, S. E., Newsome, P. T.: *J. Phys. Chem.*, **39** (1935), p. 143.

(41) Coumoulous, G. D., Crisp, D. J.: *Trans. Farad. Soc.*, **38** (1942), p. 319.

(42) Tuckett, R. F.: *Trans. Farad. Soc.*, **38** (1942), p. 310.

(43) Jones, H.: *Trans. Inst. Rubber Ind.*, **21** (1946), p. 298.

(44) Bartoe, W. F., Frederick, D. S.: *Brit. Plast.*, **16** (1944), p. 360.

(45) Lazan, B. J.: *Mod. Plast.* (Nov. 1942), p. 83.

(46) Findley, W. M.: *Mod. Plast.* (Sept. 1941), p. 57.

(47) Couzens, E. G., Wearmouth, W. G.: *J. Soc. Chem. Ind.*, **61** (1942), p. 69.

(48) Haward, R. N.: *Trans. Farad. Soc.*, **38** (1942), p. 394.

(49) Chasman, B.: *Mod. Plast.* (Feb. 1944), p. 143.

(50) Gailus, W. J., Telfair, D.: *Mod. Plast.* (May 1945), p. 45.

(51) Zinzov, W. A.: *Proc. A.S.T.M.*, **45** (1945), p. 376.

(52) Timoshenko, S.: *Strength of Materials*, pp. 173–4 (Macmillan, London, 1940).

(53) Freeman, J. G.: *Phil. Mag.*, **37** (1946), p. 855.

(54) De Bruyne, N. A.: *J. Roy. Aero. Soc.*, **41** (1937), p. 523.

(55) Schoenborn, E. M., Procter, G. R., Carvajal, J.: *Proc. A.S.T.M.*, 45 (1945), 910.

(56) Burns, R., Werring, W. W.: *Proc. A.S.T.M.*, **38** (1938), p. 39.

(57) *A.S.T.M.*: D 732–43 T.

(58) Cox, H. L., Pepper, K. W.: *J. Soc. Chem. Ind.*, **63** (1944), p. 150.

(59) Barron, H.: *Plastics*, **8** (1944), pp. 258–66; 322–30.

(60) Morey, A.: *The Strength of Materials*, 5th edition, p. 55 (Longmans, London, 1919).

(61) Smith, P. I.: *Plastics for Production*, p. 129 (Chapman & Hall, London, 1944).

(62) Nason, H. K., Lawton, T. S.: *Mod. Plast.* (Overseas Edition) (Jan. 1945), p. 45.

CHAPTER III

THE STATIC STRENGTH OF GLASS

Statistical Methods

PLASTIC materials show noticeable variations from one specimen to another when similar test pieces are broken under static forces, but the extent of such variations is, in general, comparatively small, so that significant results may often be obtained from the average of three or four tests or even from a single test. Such variations are invariably large and are inherent in glass. It is at present impossible to predict the strength of a particular piece of glass, except within very wide limits, and only the average obtained from a large number of strength measurements has real meaning. However, even an average strength figure does not alone sufficiently characterize the property measured since it is also necessary to know the degree of scatter to be expected in the results, i.e. the extent to which individual measurements are likely to depart from the mean. Thus adequate measurements of the strength of glass are inseparable from the characteristics of statistical procedure and the full implications of this variability must be appreciated before any attempt can be made to apply the conclusions reached from experimental work. However, only a few relatively simple facts about statistics need to be known, and these are easily acquired.[1, 2, 3, 4]

As a result of strength measurements on a group of glass specimens, therefore, two quantities will be obtained; e.g. if f_B the bending strength is measured, it will be accompanied by a figure for the standard deviation s, or the coefficient of variation v $\left(\mathrm{v} = \frac{s}{f_B} \times 100\,\%\right)$. The degree of scatter indicated by these quantities may be illustrated by the fact that about one in twenty of the observations will be expected to lie outside the range $f_B \pm 2s$, provided the distribution is a normal one. However, it is uncertain whether normal distributions are obtained with ordinary strength measurements on glass, though with fibres a Gaussian distribution has been reported by Jurkov,[5] but this is generally a relatively minor consideration in view of the other errors to be expected.

The Mode of Fracture of Glass

There is now wide agreement that glass breaks only under tension, and this leads to a notable simplification in its strength relations. For instance, Morey[6] states: "it is probable that in all the various methods of applying stress to glass, fracture always takes place under tension," and since his book was written the conclusion has been further reinforced. Weibull[7] made experiments on the application of stress to a circular hole in a plate and showed that the results could best be explained on the assumption that glass broke under the action of the maximum tensile stress or strain, and Poncelet[8] has shown, in experiments on the cracking of glass compressed in one dimension, that cracking occurs from the tensile stresses, arising from the state of strain. An apparent contradiction occurs when a plane glass surface is subjected to a small concentrated force and small ring cracks are formed round the circle of contact of the two objects, as reported by Raman,[9] but this mode of rupture has been investigated by Preston[10] and shown to confirm the view that glass breaks under tension. The phenomenon of ring cracks is not held to invalidate the theory that glass breaks in tension alone.

The Theory of Flaws

It is also widely accepted that the strength of glass is conditioned by the existence of flaws or weak points in the material. Here, three distinct lines of evidence support this view.

(1) The strength of massive glass as measured by bending or tension experiments is much less than that predicted by any theory which assumes that the strong intermolecular forces co-operate in a regular way.

(2) The strengths of similar pieces of glass broken in the same way vary widely, and only the average of a number of experiments is of any significance.

(3) Strength is easily affected by the treatment of the material, particularly by factors affecting the condition of the surface.

In a classical paper on the strength of glass in the massive and fibrous states Griffith[11] put forward the *flaw theory*, basing it largely on the considerations (1) and (3). He showed that glass should have a theoretical tensile strength which he derived from its heat of vaporization of about 10^6 lb./in.,^{2} but found that the practicably measurable strength with large pieces was much lower. With fibres, however, markedly higher tenacities could be obtained and he found that with fibres 0·000115 in. thick a tensile strength of 491,000 lb./in.^{2} was reached. Another interesting property was that measurements of the fibre strength immediately after the formation of the fibre gave even larger values of the tensile strength. It appears that such freshly formed glass surfaces deteriorate on keeping under normal conditions.

Griffith then went on to consider the character and mode of action of flaws in the glass; he applied the theory of stress concentration put forward by Inglis[12] to the problem of the effect of small cracks in the surface, and showed that the "theoretical" strength of glass could be reduced to that observed in practice by a scratch 5×10^{-4} in. long. Actually the strength value he used was seriously high (1,700 kg./cm.^{2}) and the scratch length to account for normal bending strengths should be larger than this. Finally, he set out to analyse the mode of rupture of glass containing scratches on its surface and made strength measurements using glass tubing that had been weakened by cracks of varying size. In his theoretical analysis he discussed the hypothesis that rupture was limited by the formation of a new surface which must take place by steps, all of which lead to a decrease in potential energy, and he obtained a relation in which the surface tension of freshly broken glass entered as a factor in strength. Thus the bending strength was represented by the relation

$$f_B = \sqrt{\frac{2E\gamma}{\pi\sigma c}}$$

where E is the Young's modulus of elasticity
γ the surface of tension
σ Poisson's ratio
c half the length of the largest crack.

By comparing the results given by his experiments with those predicted from this relation, and using a value for the surface tension of glass extrapolated down from experiments made on molten glass at different temperatures, he found that $f_B\sqrt{c}$ actually gave a mean value of 239 compared with a theoretical value of 266. Using the same theory, he estimated the tensile strength at the head of the crack, where rupture actually took place at 344,000 lb./in.,^{2} compared with a normal bending strength of less than one-tenth of this in apparently undamaged specimens.

Effect of Surface Treatment

The theory of flaws receives further support from experiments on the effects of edge and surface treatment. An early attempt was made to eliminate these points of weakness by setting the surface of the glass in strong compression and so to measure the "theoretical" strength of glass breaking internally in a bending test. Thus Littleton[13] showed that the bending strength of such a "toughened" bar could be doubled as compared with the original untreated material, but the bending strength obtained was higher in those cases with a higher initial compression and it was not established that the glass was breaking internally.

TABLE VI. EFFECT OF EDGE TREATMENT ON THE BENDING STRENGTH OF GLASS BEAMS

Treatment	Bending strength	Coefficient of variation
	kg./cm.^{2}	%
Diamond cut edges in tension	673	14·8
Diamond cut edges in compression	974	14·0
Edges ground mechanically on a stone ..	889	9·7
Edges ground and pumice polished	1,056	11·3
Fire-finished after cutting	1,033	18·8

Some interesting experiments on the effect of edge and surface treatment on the bending strength of glass beams have been made by Holland and Turner,[14] who broke groups of beams which had been subjected to varying processes (Table VI).

Clearly the strength can be greatly improved by suitable treatment, which may be presumed to modify the surface flaw pattern of the glass. On the assumption that the glass was weakened by the presence of small cracks, they examined the visible depth of the cracks obtained under differing conditions and plotted the relation between depth and breaking strength (Fig. 15).

These results, as presented by Holland and Turner with a linear dependence of strength on scratch depth, are not in agreement with the equation of Griffith; the apparent contradiction could be resolved by distinguishing between the visible flaws of Holland and Turner and the small cracks, whose length is only indirectly related to them, which actually determine the strength of the glass. It will be seen that Holland and Turner's observations separated into two groups, according as to whether only the sides, or both the sides and edges, were subjected to a specified treatment, and viewed thus the relation between measured crack depth and bending strength appears to be approximately linear. Both lines tend to a value of about 1,000 kg./cm.^{2} when no visible cracks are present, but it is also found that under these conditions there is no observable tendency for the breaking of the glass to become more uniform, i.e. for the coefficient of variation to decrease. This result suggests that flaws still determine the rupture properties even when they cannot be readily seen. It appears that 1,000 kg./cm.^{2} is the order of strength to be expected when a massive soda-lime-silica glass is broken by a straight forward bending system at a polished or fire-finished surface with no visible flaws. For instance, a pane of glass can be broken at the centre by simply supporting it and subjecting it to a central load, when the maximum bending stress is given by the relation[15]

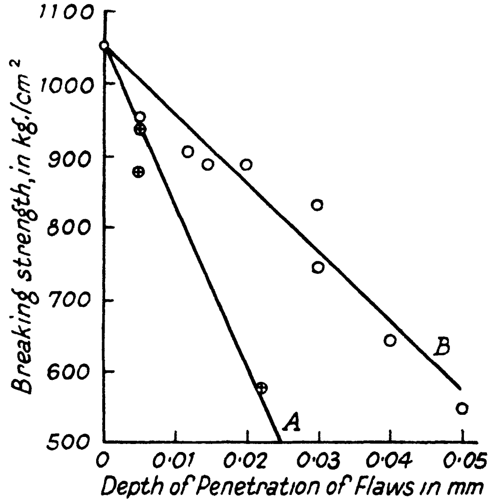

FIG. 15.—The relation between the bending strength of a glass beam and the visible depth of the cracks at the edges.[14]

$$f_B = \frac{P(\text{max.})}{h^2}\left[(1+\sigma)\left(0{\cdot}485\log_{10}\frac{2a}{\pi h}+0{\cdot}52\right)+0{\cdot}48\right]$$

where P (max.) is the maximum central load
h the thickness
a the length of the side of the square pane.

In this way Haward[16] found values of 1,000 to 1,360 kg./cm.^{2} for the bending strength of sheet glass in agreement with earlier experiments by Graf.[17] Experiments by Mangler[18] have shown that the direction of drawing in sheet glass has little effect on the tensile strength of specimens cut parallel and normal to the direction of drawing.

Apart from the effects of grinding and polishing, the bending strength of glass can be affected in many other ways. Jurkov[19] has shown that the strength of silica glass fibres baked out and broken *in vacuo* is 3½ to 4½ times greater than in air, and Preston[20] has reported that with large humidity changes considerable changes in strength occur with massive glass. Other experiments by Boow and Turner[21] have shown that under certain conditions the sulphur dioxide present in furnace gases can have a favourable effect on strength, while Jurkov[5] has shown that strength is improved by etching the surface of the glass by hydrofluoric acid.

There has been a good deal of discussion as to the reality or otherwise of the cracks required by Griffiths to account for the measured strength of apparently undamaged glass. Some attempts to find them by microscopic methods or by the absorption of anthracene from benzene solutions[22] failed, and though Andrade and Tsien[23] showed that lines of preferential absorption of sodium vapour existed on glass surfaces, and increased markedly in the first 48 hours after the surface was formed, i.e. the period Griffith reported a decline in fibre strength, the precise significance of their results is open to doubt. Poncelet[8] has suggested that the flaws only come into existence after the application of a stress, but this hypothesis also awaits confirmation. Obviously it is possible to conceive of the narrow cracks suggested by Griffith, which, though wide compared with intermolecular forces, are too narrow to be detected by microscopic examination, but until their existence is proven the precise nature of the flaws or molecular disarrangements which limit the strength of massive glass must remain uncertain.

Strength of Massive Glass as a Function of Form and Size

It is a necessary consequence of the theory of a wide variation of flaw severity in glass that a particular strength value cannot be assigned to a particular type of glass. If specimens of the same glass having different dimensions are broken, the bending or tensile strengths will be found to vary. This property has been shown experimentally by Holland and Turner,[14] who demonstrated that the bending strength of a glass beam depended upon the width, and others[16, 24] have shown that bending strength is decreased as the thickness of a beam or plate is increased. In tensile tests Smekal[25] has established a similar effect with rods of 0·3 to 4·0 mm.^{2} cross-section.

The work of Holland and Turner is included in a general survey of the strength of glass by Bailey,[26] who puts forward a theory of the strength-area relation, i.e. a theory relating the measured strength of a glass specimen to the area of the glass surface under stress. This theory is based on four point bending tests on 103 glass rods whose breaking yielded the following figures under the usual statistical treatment (Table VII).

TABLE VII. STRENGTH OF THE STANDARD RODS CHOSEN BY BAILEY

Mean bending strength	11,350 lb./in.^{2}
Standard deviation (s)	1,623 lb./in.^{2}
Standard error of mean	160 lb./in.^{2}
Rate of application of stress	3,200 lb./in.^{2}/min.

Bailey then considers the case of a rod under tension which breaks when the strength of its weakest flaw ($f_T a$) is exceeded. If, however, the rod were broken in half and the two pieces broken, one piece containing the weakest flaw would break at a stress $f_T a$, the other at a higher strength $f_T b$. The average strength of the two rods will be

$$\tfrac{1}{2}\,(f_T a + f_T b) > f_T a$$

Similarly if the rod were cut into n pieces the strength would be f_T

where $$f_T = \frac{1}{n}(f_T a + f_T b + f_T c + \ldots)$$

and $$f_T a < f_T b < f_T c$$

Also for the n pieces the average stressed area will be

$$A_n = \frac{L}{n}(2\,\pi\,R) \qquad R = \text{radius of the rod of length } L.$$

i.e. as n increases A decreases and the average strength increases.

Bailey then shows that if two glasses have the same flaw pattern but are broken with differing areas under stress, the results may be related statistically.

For instance, if in the case of the standard group of rods the glass had been broken with twice the area under stress, the result would be the same as if the rods had been averaged by choosing the weaker rod out of pairs chosen at random, and similarly for larger groups of rods. Mathematically this problem is the same as that of calculating the strength of chains of a given length made up of links of differing strength, when the strength of the whole chain is that of the weakest link. Bailey takes his rods and calculates what the strengths would be if the weakest rods out of groups of varying size were chosen; this corresponds with breaking glass of the same flaw pattern with increasing surface areas under stress (Table VIII).

TABLE VIII. STRENGTH OF THE WEAKEST ROD IN A GROUP

	Number of rods in group	Average strength of weakest rod	Remarks
	1	11,350	Average strength in tests
Equivalent to increasing surface area under stress	2	10,424	Calculated
	10	8,805	Calculated
	50	7,480	Calculated
	103	6,895	Lowest value found

In order to correlate the strength-area relation for different experiments with the same flaw pattern two further steps must be taken. Firstly, an assumption must be made to enable the area under stress to be measured, and for this purpose Bailey chooses that area where the stress is above 96·5 per cent of the maximum stress. Secondly, an empirical method based on the results of Black[27] is used to eliminate the effect of different rates of stressing at the apex of the weakest flaw. In this way he calculates the strength of Holland and Turner's glass[14] if it had the same type of flaw pattern as his rods, and shows that differences in their results are partly to be explained by differing rates of stressing.

Nevertheless, although Bailey's theory appears to be successful in dealing with the case of bending and tensile tests with massive glass, he shows, by analysing the results of Gooding,[28] that an extrapolation of his strength-area relation cannot account for the high strength of glass fibres except in the case of the thickest and weakest samples. This is in agreement with Murgatroyd,[29] who concluded that the behaviour of fibres was fundamentally different from that of massive glass.

However, this point of view is not accepted by Preston,[30] who made experiments on small areas of massive glass in which bending strengths of ca. 10,000 kg./cm.^{2} were obtained. These results are described in Chap. V, and, in conjunction with Bailey's observations, they suggest that the area strength relation for very small areas cannot be readily deduced from larger scale experiments.

The theory put forward by Bailey,[26] which was worked out for the specific case of glass, has much in common with Weibull's *Statistical Theory of the Strength of Materials*.[31] As with Bailey, the dispersion of results obtained in strength measurements is made the basis of a theory relating the size of the test piece to the probability of rupture under a given stress distribution. In this case, however, the volume, v, of material under stress is made the basis of computation, and an attempt is made to relate the probability of fracture p to the applied stress pattern by a relation of the following form:

TABLE IX. COMPARISON OF THE RESULTS OF HOLLAND AND TURNER WITH THOSE PREDICTED BY THE THEORY OF BAILEY

1 Width of test pieces	2 Strength of Bailey's rods if they had been of such a size as to have the same stressed area as in Holland and Turner's experiments	3 Col. 2 corrected for the different rates of stressing used by Holland and Turner	4 Experimental figures obtained by Holland and Turner
cm.	lb./in.^{2}	lb./in.^{2}	lb./in.^{2}
0·40	14,500	18,400	18,400
0·485	14,100	17,400	17,400
0·73	13,500	16,100	15,800
0·775	13,400	15,900	14,600
0·945	13,100	15,200	14,100
1·19	12,700	14,400	13,300

$$\log(1-p) = -\int_v F(S)\,dv$$

and it is further found empirically that in a number of cases a function $F(S)$ of the following form may be applied:

$$F(S) = \frac{(S-S_u)^m}{S_0}$$

where S_u, S_0 and m are constants of the material. Thus the size dependence of the strength of glass may be seen in relation to the behaviour of other materials. For example, the case of cast iron, taken from the work of Campbell,[32] is illustrated in Table X.

TABLE X. TENSILE STRENGTH OF VARIOUS SIZES OF CAST-IRON BARS

Diameter, in.		Tensile strength
Nominal as cast	Reduced section	
		lb./in ^{2}
0·25	0·1875	50,800
0·375	0·253	38,100
0·625	0·400	32,200
0·875	0·505	26,000
1·20	0·80	23,000

Another instance of this type of material is furnished by concrete. Here again there is a marked dependence between the size of the sample and the average value obtained in strength measurements. In this case a theory has been developed by Tucker,[33] who makes use of Tippet's tables[34] relating the probability of the occurrence of extreme individuals in samples of a normal population. In this way Tucker estimates the strength of large pieces of concrete from experiments based on the breaking of a number of smaller specimens.[35]

From these examples it is clear that variations in strength measurements with the size of the samples under test are of widespread occurrence and may well prove to be of more general application than is at present realized. The differences in the present theories, apart from the question of relating the occurrence of the weakest link to the volume or the surface area of the sample, are a question of mathematical treatment rather than of fundamental approach, and similar qualitative predictions are made in all cases. For instance, it is to be expected that with any size sensitive material, if like samples are tested in bending or tension, the bending tests will give the higher results, since in this case the area (or volume) under maximum stress is smaller than in tension. This result is normally obtained with glass.

Effect of Composition on Bending and Tensile Strength

The most systematic experiments on the effects of composition on strength have been carried out by Gehlhoff and Thomas,[36] who made bending and tensile strength measurements with glass rods and also crushing strength determinations on polished glass plates.

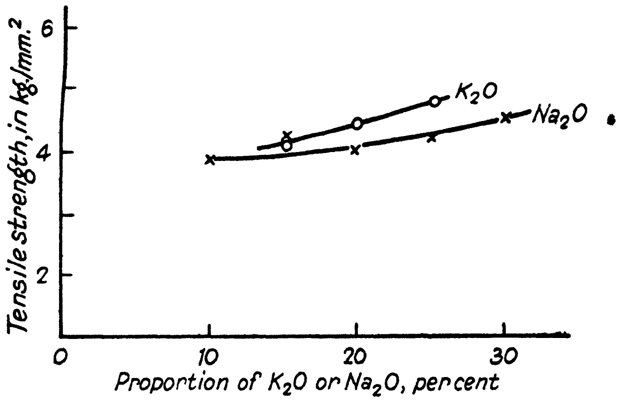

FIG. 16.—The effect of the addition of alkali oxides on the tensile strength of standard soda glass rod.[36]

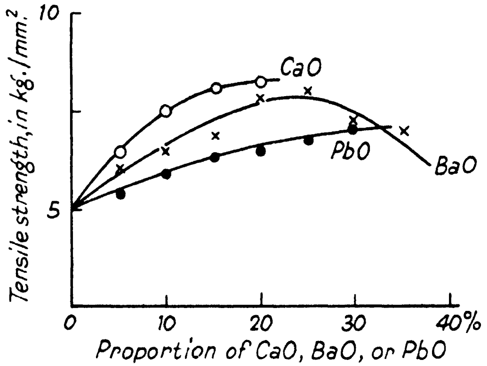

FIG. 17.—The effect of certain metallic oxides on the tensile strength of standard soda glass rods.[36]

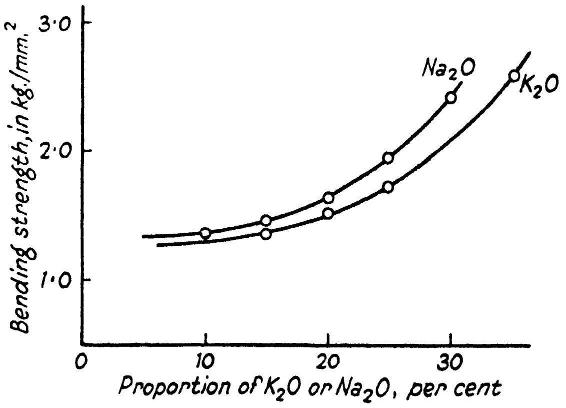

FIG. 18.—The effect of alkali oxides on the bending strength of standard soda glass rods.[36] (Actual figures should be multiplied by 8.)[37]

They took as their starting point a glass of composition 0·18 Na_2O, 0·82 SiO_2, and investigated the effect of replacing SiO_2 by polybasic oxides, the effect of Na_2O and K_2O on silica being investigated separately. Their results for certain oxides (Figs. 16, 17, 18, 19) illustrate the considerable increase in strength when CaO is introduced. The results show higher values for bending strength than tensile strength, but Greene[37] has shown that the figures for bending strength must be multiplied by 8, and when this correction is made the usual higher results for bending, as against tensile tests, are obtained.

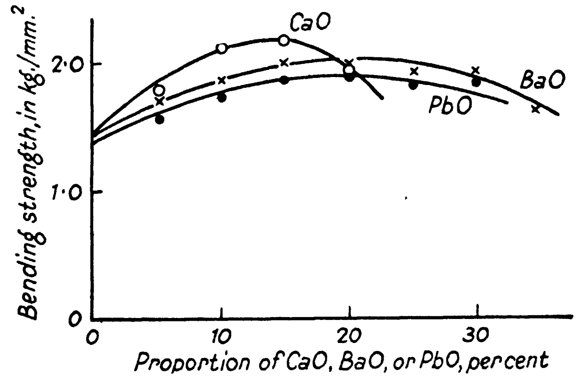

FIG. 19.—The effect of certain metallic oxides on the bending strength of standard soda glass rods.[36] (Actual figures should be multiplied by 8.)[37]

Earlier experiments on the effects of varying composition have been carried out by Winkelman and Schott,[38] and a more detailed discussion of the whole topic is given by Morey.[6]

Effect of the Rate of Application of Stress on Static Strength

It has been clearly established that the results obtained in bending or tensile tests strongly depend on the rate of application of the stress or upon the time in which the glass is broken. This appears to apply to many different methods of testing at normal temperatures. The most complete range of results, covering a factor of 10^7 in time, has been published by Preston[20] (Fig. 20). Over this wide range of time the bending strength increases by a factor of slightly more than 3, a result in general agreement with bending experiments by Graf,[39] Preston,[40] Holland and Turner,[41] and Black.[27] This time effect on static fatigue is not confined to any particular type of test, and the existence of similar phenomena has been demonstrated by Haward[16] for panes of glass under central load, by McCormick[42] for the bursting of glass bulbs, and by Apelt[43] for tensile tests on glass rods.

The occurrence of such a time factor has naturally led to numerous attempts at explanation and correlation, though a satisfactory and generally accepted theory does not yet exist. In these circumstances purely empirical descriptions may be extremely useful, and for this purpose both Harries[44] and Holland and Turner[41] have put forward equations of the type

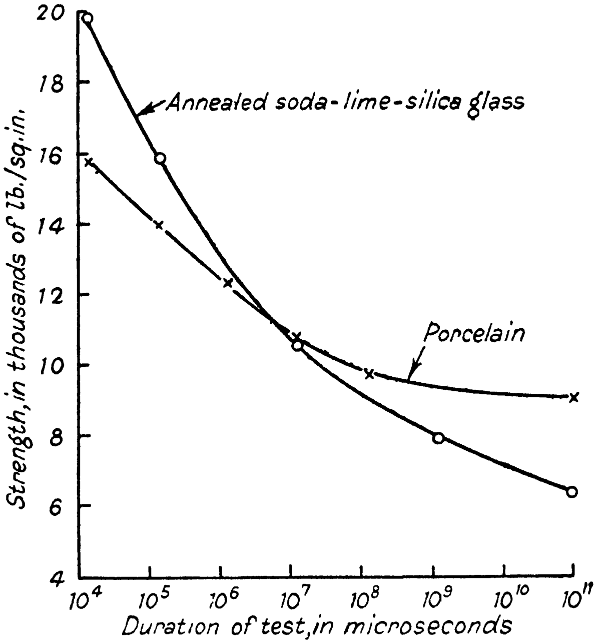

FIG. 20.—The effect of the fracture time on the bending strength of soda glass and porcelain.[20]

$$\text{Strength proportional to } \left(\frac{1}{\text{time}}\right)^{\frac{1}{\gamma}}$$

where γ is empirically determined.

Harries obtained an average value of 11·9 for γ from the consideration of a group of published results, and Holland and Turner derived a figure of 12·8 from their own experiments. There seems no reason to doubt that the effect of time in the breaking of a soda-lime-silica glass can be roughly represented by a relation of this type, which may be employed as a useful approximation for practical purposes. However, a more thorough theoretical understanding of the whole process of rupture is needed, particularly as the existence of an unexplained time element introduces an element of doubt into other strength measurements. An important difficulty here is that, although the existence of a time factor in the breaking stress has been very widely observed, no agreement exists as to whether or not a slow deformation of massive glass always occurs simultaneously at ordinary temperatures.[45] As an example of the differing points of view, Preston[20] holds that the viscosity of glass is so high that no real meaning can be attached to it; slow deformations are therefore absent, and glass may be regarded as a perfect solid; but Murgatroyd and Sykes,[46] in some recent experiments, claim to have measured slow deformations amounting to 1 per cent or less of the total Hookean deformation. Obviously, explanations put forward to account for the time factor in fracture may be affected by whatever views are held on the subject of slow deformation.

Theory of Static Fatigue in Glass

The view that static fatigue is connected with the action of an adsorbed film on the glass is held by Orowan,[47] Preston,[20] and Rehbinder.[48] Orowan[47] considers that the problem should be treated by a further development of the Griffith theory of flaws. He notes that, in the case of mica, the surface tension of the solid phase (γ) is reduced by a factor of about 10 in the presence of air or moisture as compared with a vacuum. Since the Griffith theory requires the strength to be proportional $(\gamma)^{\frac{1}{2}}$, it follows immediately that if glass behaves in a similar way there should be a difference amounting to a factor of about 3 in the strength of glass according to whether it is measured in equilibrium with moist air or in a vacuum. Orowan notes that the results of different workers[20, 41] show a total range of variation in the breaking stress of the same magnitude, and concludes that the time effect is to be explained by a slow reduction of the surface tension as an adsorbed film diffuses on the surface of the glass. Finally, he predicts there will be no static fatigue effect when glass is broken in a vacuum.

On the qualitative nature of the processes involved in static fatigue Preston[20] generally supports Orowan; in particular, he has investigated the way in which the time element in fracture varies with the temperature. This can be done by plotting the ratio of the strengths measured with fracture times of 0·1 and 100 sec. at a series of temperatures. The results show that the time effect is small at extreme temperatures, but reaches a maximum between 50 and 300° C. (Fig. 21). These experiments are interpreted by Preston as follows: at the lowest temperatures the glass is but slightly time-sensitive owing to the small mobility of the adsorbed film, and above 200° C. this film is gradually removed by evaporation and the glass again becomes less time-sensitive in fracture. In between these two extremes there is a point where the time factor has a maximum effect.

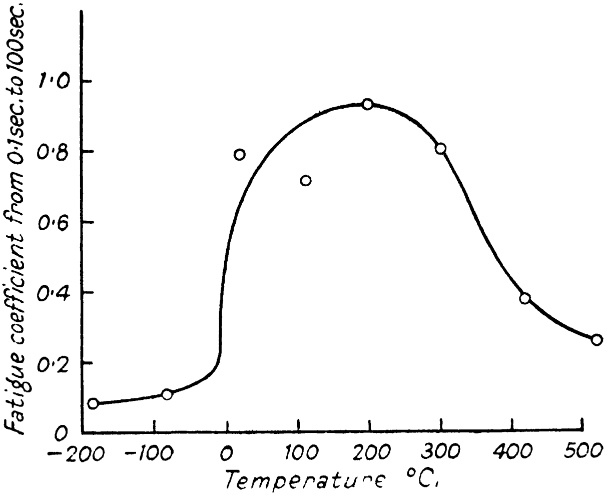

FIG. 21.—The static fatigue coefficient of glass plotted against temperature.[20]

In another paper Preston and Baker[49] specifically investigated the question of whether there is a time factor when glass is broken in a vacuum. Two groups of rods, which had been baked out at 300° C. and 0·1 micron mercury pressure, were tested at different rates of stressing, and the results showed that the bending strengths were the same for breaking times of 0·1 and 10 sec.'Preston and Baker therefore concluded that static fatigue did not occur in the absence of adsorbed films.

A third and somewhat similar approach to the same question is provided by Rehbinder[48] in an article in which he reviews recent work carried out in the U.S.S.R. on the subject of the effect of external agents on the mechanical properties of metals and other materials. He suggests that many of the effects associated both with deformation and fracture can be explained by assuming that surface active substances can penetrate the surface of a strained solid along wedge-shaped ultra-microscopic cracks that are developed in the process of deformation. When the stress is removed the cracks gradually close and the adsorbed materials are expelled. In support of this view the example is given of the deformation of mica. It is stated that when a sheet of mica is bent in absolutely dry air the deformation takes place almost at once and is immediately reversed when the stress is removed, but when water or alcohol is present both processes take place gradually. Thus, according to Rehbinder, both deformation and fracture are controlled by the slow diffusion of adsorbed substances.

A reduction in strength under the action of external agents has been well established in a number of investigations carried out with metals. Gough,[50] and Gough and Sopwith[51] have emphasized the importance of atmospheric oxygen in the measurement of fatigue strength in metals subject to alternating stresses. It was shown that when tests were carried out *in vacuo* there was an improvement in fatigue strength, the maximum increase being 26 per cent in the case of a 70 : 30 brass. More recently Evans and Simnad[52] have shown that the rate of corrosion of metals is markedly increased when the surface is subjected to a stress in a corroding medium. Thus the two processes of fracture and corrosion appear to reinforce each other.

We may conclude that there is fairly strong evidence in favour of the theory that adsorbed films play a vital part in static fatigue in glass, but this theory at present lacks a quantitative development which would allow a precise comparison with experimental results. In this connection it has been shown by Haward,[53] and by Preston,[54] and by Preston and Glathart,[55] that if $\log t/f$ or $\log t$* is plotted against $1/f$, where f is the stress required to fracture the glass in time t, an excellent straight line is obtained (Fig. 22). These two quantities do not give sensible differences in plotting since changes in f are small compared with t. These points, taken from the work of Preston,[20] cover the widest range of time investigated up to the present and no deviation from linearity is observable at either end.

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* These two quantities are not sensibly distinct since variations in t are large compared with f.

The question therefore arises whether the same relation will apply outside this time range. On the whole it must be doubted whether the line may be extrapolated to shorter times, since, as pointed out by Preston,[54] this would require the strength of glass to be infinite at time below 6 microsec. In this connection the theoretical treatment given by Haward,[53] although containing some rather doubtful assumptions, may be of interest in that it indicates how a good linearity of the log t–$1/f$ relation in the range investigated may be reconciled with the assumption of a finite short time strength. The treatment involves the use of a simple exponential term for the probability of a particular stress in a fluctuating field. Another line of approach by which the log t–$1/f$ can be theoretically derived from a treatment of the effect of mechanical stress and moisture on the orientation of an atomic network is at present being developed by Taylor,[56] but only a summary of the theory has so far been published.

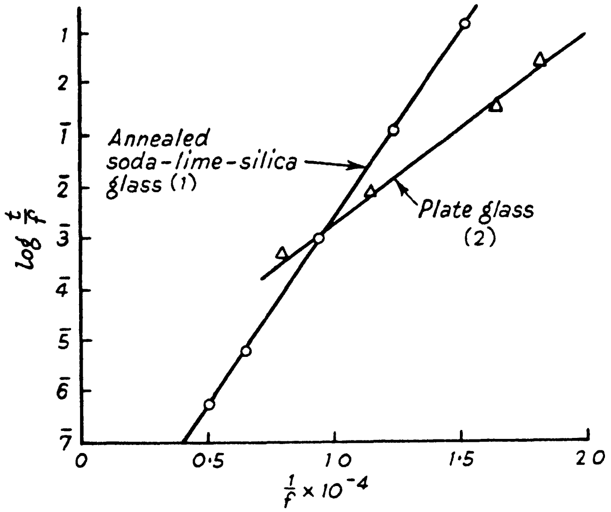


FIG. 22.—Preston's results for the time factor in glass fracture plotted in the form $\log \frac{t}{f} - \frac{1}{f}$ [53]

The figures for the soda-lime-silica glass are the same as those in Fig. 20.

Thus there is still no direct link between the theories of moisture-absorption of Orowan, Preston, and Rehbinder and the log t–$1/f$ relation of Preston and Haward, but a different theory leading to this relation has been evolved by Murgatroyd. In his first papers[22, 57] he developed a theory of the time factor in the fracture of glass in terms of an empirical treatment of the relaxation of a quasi-viscous material assumed to be present in the glass. According to this view, the stress is increasingly thrown on the more rigid parts of the material by the slow deformation of a viscous component until fracture occurs. Since the deformation is held to be reversed when the stress is removed, the theory suggests that glass should not be permanently weakened by a stressing operation. Experiments by Murgatroyd and Sykes,[58] where it was shown that the remaining glass rods were not sensibly weakened by a stressing operation in which 20 per cent of a sample were fractured, are therefore considered to support this theory. In a later paper[46] the slow deformation of glass at room temperature was investigated, and it was claimed that very small time-dependent deformations could be observed which were proportional to the log. of the time. Finally Murgatroyd and Sykes[59] have shown that the original form of the viscous pocket theory can be modified so that the $\log t\text{–}1/f$ relation is directly obtained from the logarithmic character of the deformation process. Thus it appears that at present the $\log t\text{–}1/f$ relation can be derived most directly by a theory which seems to take no adequate account of the evidence regarding the effect of adsorbed materials.

Finally it should be noted that other methods of treating static fatigue have been put forward by Bailey,[26] who develops an analogy between the behaviour of metals and glass, and by Gurney,[60] who considered the effect of stress on the vapour pressure of a glass and examined the possibility of evaporation from points of stress concentration. Gurney found that such factors could only account for a part of the observed effects and concluded that atmospheric attack was also an important element in the process. Obviously, the existence of more than one factor causing static fatigue in glass is possible in the light of the present evidence, though the occurrence of a simple quantitative relation between stress and fracture time suggests a single process. That this process is connected with the action of adsorbed moisture seems most likely on the present evidence.

The Variation of the Strength of Glass with Temperature

This topic has been investigated by Smekal,[61] Mengelkoch,[62] Vonnegut and Glathart,[63] and Preston[20] whose results, together with certain comparative figures for steel, are given in Fig. 23.

The conclusions of all three workers are in general agreement. The strength of glass is dependent on temperature and reaches a minimum round 200° C., but with extreme cold or above 300° C. perceptible improvements are obtained. However, some recently published experiments by Jones and Turner,[64] carried out on fire-finished glass beams under carefully controlled conditions, gave a constant bending strength throughout the temperature range 20 to 450° C. A part of this apparent discrepancy has been resolved by Holland and Turner, who obtained an increase of strength at a temperature of − 40° C.

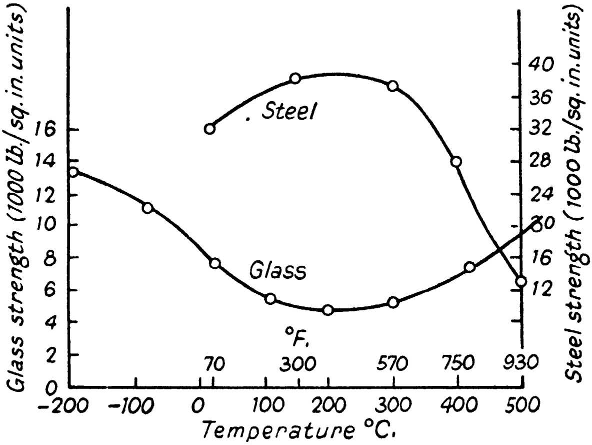


FIG. 23.—The effect of temperature on the strength of glass and steel.[20]

Jones and Turner's results seem to contradict those of Preston, but it must be remembered that there are a number of factors still to be explored, and the temperature variation might depend markedly on the conditions of testing. Indeed, as far as the time factor is concerned the curve shown in Fig. 21 clearly predicts considerable differences in the temperature-strength relation according to the rate of stressing chosen in the experiments, and other variations could be introduced by size factors and by the finish of the test piece. However, since the scale of all the variations reported is only large over wide temperature ranges, it may be concluded that in normal temperate conditions the strength of glass is not greatly affected. In particular, it seems safe to assume that, except in the temperature range 100 to 300° C., glass is at least as strong as at room temperature. The results of

Jones and Turner confirm those of Preston, namely, that glass is more able to withstand sustained loading above, say, 300° C., but in contrast with Preston's results given in Fig. 21, they conclude that this improvement is a continuous one above 20° C.

The Cracking of Glass

The typical behaviour of breaking glass must be familiar to most people; as soon as rupture commences cracks spread rapidly and the elastic energy stored in the glass is suddenly and explosively released. It now appears that the velocity, or at least the maximum velocity, at which these cracks can travel is a constant characteristic property of the glass. The phenomenon has been investigated by the methods of spark photography under two widely differing conditions: Schardin and Struth[65] examined the case of a bullet impact on glass, and Edgerton and Barstow[66] investigated the breaking of panes of glass under a central force using a ball and spring arrangement. In both cases a velocity of crack propagation of 5,000 ft./sec. was obtained. Edgerton and Barstow went on to measure the velocity of transmission for transverse and compression waves in the glass and found values of 11,000 and 18,000 ft./sec. respectively, which are in agreement with the known elastic constants and with the results of Baird,[67] but which appear to be unrelated to the cracking velocity. Two of their photographs are given on Plates I and II, and they illustrate the remarkable circular form given by cracks spreading from a point in fractured glass.

A qualitative theoretical explanation of this constant velocity of crack propagation has been put forward by Poncelet.[8] He considers that these experiments really measure the *maximum* velocity of crack propagation which is a constant for the material, though cracks may travel more slowly. When cracking takes place there is a tendency for the stress at the tip of the advancing fissure to increase, and as this occurs the crack velocity increases too, until, at a certain critical stress, forking occurs and the velocity is kept within a maximum figure. In the same paper Poncelet shows that the same hypothesis can be used to explain the results of Smekal, Muller *et al.*[25, 36, 68, 69] concerning the breaking of glass rods under tension. Smekal found that the broken area of glass rods fractured under tension could be divided into two parts: a "mirror" area *A* where the surface of the glass was smooth, and a rougher part. If a series of similar rods were broken, the total mirror area could vary from 5 to 40 per cent of the total cross-section of the rods, and the observed tensile strength also varied, but not independently of the mirror area. It was found that if q was the total cross-sectional area of the rod, then

$$\text{Tensile strength} = \text{constant}\,(1 - A/q)$$

Poncelet[8] shows that these results would follow immediately from his theory if the mirror area was caused by that part of the fracture process in which the rate of cracking was increasing and the rougher surface by the part where forking occurs. Although this point of view is attractive, it now appears that it cannot be fully accepted, since more recent evidence has shown that the maximum velocity of cracking can be reached under suitable conditions when the mirror area is only one-fifth complete.

The theory of a critical forking stress is also supported by various observations on the amount of cracking and tearing taking place in glass and clay plates and rubber sheets. In a number of papers concerned with the rupture of these materials a common similarity has been reported, in that when they are broken under differing conditions those samples which are strongest, or are subjected to the most severe impact, also suffer the largest amount of cracking. In the case of clay, plaster of Paris, and sealing-wax plates, Suzuki[70] demonstrated that the number of pieces into which the plate is broken under impact with a given weight increases with the height from which the weight is dropped. With glass, Gehlhoff and Thomas[36] observed in the course of their impact experiments that the stronger pieces were broken into a larger number of fragments than the weaker ones, while Haward[53] found that similar effects occurred with glass plates under impact and static loading as shown in Plates III and IV.

That there should be a similarity of behaviour between glass and clay is not surprising, but it is of particular interest that similar phenomena have been reported by Treloar[71] in the case of bursting tests with rubber sheets. Treloar found that when rupture occurred in a bursting test numerous petal-like shapes were formed radiating from the point of rupture in a manner suggesting a similarity to cracked glass. Using a series of rubbers of differing tensile strength, he found that there was a relation between the number of petals formed and the strength of the material. The explanation put forward by Treloar that the effect is connected with the high modulus of elasticity of the stronger rubbers under the conditions of rupture appears to be excluded by the analogy with glass, since the modulus of elasticity of glass is independent of the stress. The correlation would appear to be between either the stress at rupture or the energy stored in the material and the number of petals and cracks. In these cases an explanation on the lines of Poncelet's critical forking stress would again appear to be applicable.

Toughened Glass

If a sheet of glass is quickly cooled from a high temperature the outer layers of glass cool first while the centre is still hot and therefore soft. When the centre cools and contracts the outer layers of glass are set in strong compression and the whole glass is in a permanent state of strain. The increased bending strength of this heat-treated glass has already been mentioned in connection with the work of Littleton, whose general explanation of its behaviour, that the state of compression of the surface layers inhibits rupture in tension, is now widely accepted.

It follows that for most purposes the bending strength of toughened glass may be represented by the relation:

$$f_B \text{ toughened glass} = f_B \text{ sheet glass} + K$$

where K is a constant representing the average compressive stress in the surface of the glass which must be reversed before the glass can be broken in tension. The same relation would apply to the tensile strength of toughened glass rods provided the glass breaks from surface flaws only, and for this reason theories of the strength of toughened glass are closely connected with whatever views may be held on the possibility of rupture beginning at internal flaws. Littleton and Preston[72] assume that the difference between an internal and a surface flaw is that the former has to be extended in *two* directions when rupture occurs, whereas the surface flaw has only to extend in one direction, and so the internal strength of glass is double the surface strength. From this conclusion it follows that there is a theoretical limit for the most useful degree of toughening, since an increase in tension at the centre of the glass beyond a certain point will have a weakening effect. However, the effect is not the same for bending and tension, and by analysing the stress distributions it is shown that the effect of toughening should be much greater in bending than in tension, namely:

Maximum tensile strength of a toughened rod should be $1 \cdot 5 \times$ annealed rod.
Maximum bending strength of a toughened beam should be $3 \cdot 4 \times$ annealed beam.

With the further assumption that the distribution of thermal stresses is parabolic, the relation between the bending strength (modulus of rupture) and degree of toughening is worked out theoretically (Fig. 24).

Experimental bending tests are then related to the theory by measuring the strain by the method of birefringence together with the bending strength, and in this way the experimental points are obtained. The theory, although necessarily approximate, is borne out by the experiments in that a maximum strength is obtained under the predicted strain, but more evidence is needed on the descending portion of the curve, particularly as there is so little other evidence concerning the occurrence of internal breakage in glass.

Indeed, experiments by Holland and Turner,[73] in which the curvature of splinters produced from the surface of toughened glass was measured, lead to the conclusion that the maximum internal tension of certain specimens of toughened glass varied from 1 to $5 \cdot 3 \times 10^4$ kg./cm.,^{2} a value far above the figure of Preston and Littleton, and one which, if correct, is incompatible both with the conception of internal strength put forward by the latter and with their explanation of the limiting strength to be obtained by the best tempering treatment.

The question whether toughened glass breaks from the surface is also important in relation to the theory of the time effect put forward by Orowan,[46] that toughened glass breaking internally should show no time factor since no diffusion of an adsorbed film could be postulated. On the other hand, if toughened glass still breaks from the surface it should also show a reduced relative time factor as compared with ordinary glass even if the adsorbed layer theory of the time factor is correct, since K in the equation (p. 60) will be constant with time, and the changes in bending strength should be, therefore, numerically equal in each case. The results of bending tests on toughened and sheet glass carried out by Haward[74] are given in Table XI, and it will be seen that they favour the view that the toughened glass breaks from the surface and shows a small time factor numerically similar to that of sheet glass. The implications of these results are of course in disagreement with the theory of Littleton and Preston.[71]

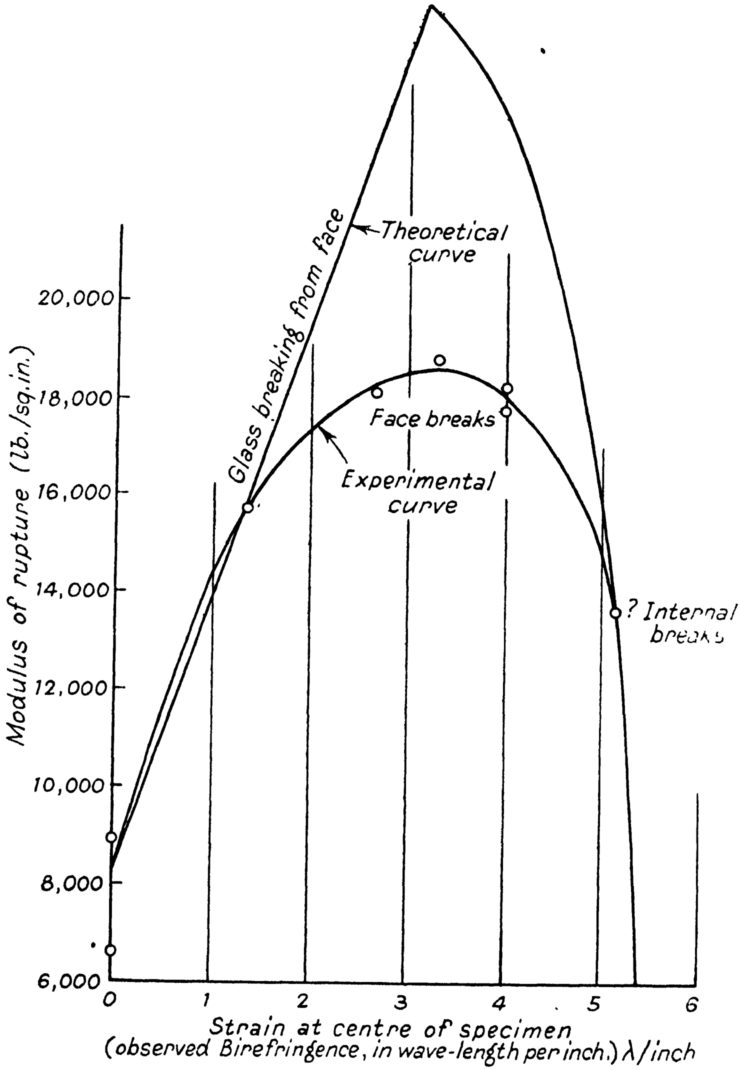


FIG. 24.—The bending strength (modulus of rupture) of toughened glass plotted against the observed strain at the centre of the test piece.[72]

In toughened glass the sum of the outer compressions must be numerically equal to the tensions produced in the inner layers of glass, so the degree of toughening will be affected by the relative rates of cooling of the inner and outer parts of the glass, in which geometry, the heat conductivity of the glass, and conditions of cooling will all play their part. These factors lead to a difficulty in producing thin toughened glass, since the outer cooling is rapidly transmitted through the sheet and large differences in rate of cooling are not readily produced. For this reason most commercial toughened glass is 3/16 in. or more thick. The thicker the glass the easier it is to produce a large value of K, and so the ordinary tendency of glass to give a lower bending strength with thicker material is reversed in toughened glass and the practically attainable bending strength increases with thickness as illustrated by the following figures of von Reis:[75]

TABLE XI. BENDING STRENGTHS OF SHEET AND TOUGHENED GLASS SQUARES UNDER A CENTRAL FORCE AT DIFFERENT RATES OF STRESSING

Average thickness	Average time	Average force	Bending strength $f_B \pm 2s/\sqrt{N}$	N number of tests	Coeff. of variation $v = s/f_B$
cm.	sec.	kg.	kg./cm.^{2}		%
Sheet Glass					
0·405	2,160	62·4	730 ± 70	28	25
0·406	180	79·6	930 ± 77	30	23
0·407	23	84·6	990 ± 70	30	19
0·406	1·8	96·6	1,140 ± 100	30	25
Toughened Glass					
0·467	2,260	239	2,070 ± 92	36	13·4
0·462	201	246	2,180 ± 93	37	12·9
0·464	26	257	2,260 ± 91	36	12·1
0·464	2·2	290	2,550 ± 107	44	13·9

Absolute difference due to time factor:	Sheet glass	410 kg./cm.^{2}
	Toughened glass ..	480 kg./cm.^{2}

Thickness	5	8	12 mm.
Bending strength ..	2,000	2,500	3,000 kg./cm.^{2}

When toughened glass is broken it is invariably shattered into a large number of pieces, giving the typical breaking pattern shown in the shattered part of Plate I. For this reason it is impossible to cut this material, and toughened glass must be fashioned in the form in which it is to be used. Its elasticity is the same as that of ordinary sheet or plate.[75]

Other Strength Properties

The strength measurements outlined do not include all the types which it may be of practical importance to investigate; among them are the bursting strength of fashioned glass articles, and crushing strength. Nevertheless, as has been pointed out by Poncelet[8] and Preson,[76] it is probable that even under crushing stresses glass breaks in tension. If this view is accepted, it should follow that all these measurements are really varieties of bending or tensile tests complicated by elaborate geometry, and that they should be subject to the fundamental properties of the bending strength of glass together with the particular variables involved in specific tests. For example, experiments on the bursting pressure of lamp bulbs have been recorded by McCormick,[42] and they show a time factor similar to that obtained in ordinary bending tests; an interesting feature was that, in one instance, frosted glass bulbs gave higher bursting strength values over a series of times than clear glass.

TABLE XII. CRUSHING STRENGTH OF GLASS AS MEASURED BETWEEN DIFFERENT TYPES OF METAL PLATE[77]

Plate	Crushing strength
	kg./cm.^{2}
Tin	3,920
Copper	6,580
Polished steel	12,640

The early work of Winkelman and Schott[77] on crushing strength measurements showed that results of this type were markedly affected by the manner in which the crushing stresses were applied; for instance, when glass is crushed between different types of plate, different values of the crushing strength are obtained (Table XII).

The results were also affected by the precise condition of polishing of the steel plates. Generally speaking, Winkelman and Schott found that with 6 mm. cubes of glass and polished steel plates the crushing strength was 10 to 20 times the tenacity of the same glass. This result is confirmed by the work of Gehlhoff and Thomas,[36] who used 4 × 4 × (1½–2) mm. test pieces and also polished steel plates together with a series of glasses of different composition. The values obtained for the crushing strength were all fairly close to 10,000 kg./cm.^{2} and the effects of changing composition were not very large. However, they were measurable and were not always in the same sense as those which occurred with bending strength. For instance, the addition of Na_2O, K_2O or CaO (up to 20 per cent) increased the bending and tensile strengths but reduced the crushing strength. This is, perhaps, surprising, but it does not necessarily invalidate the hypothesis that rupture occurs under tension, since many properties may be involved in bringing this tension into play. On the other hand, the generally high values of the crushing strength of glass support the view that the glass breaks in tension only, since the compression of a cube between two flat surfaces obviously represents a highly inefficient way of applying a tensile stress to a glass surface.

REFERENCES—III

(1) Evans, U. R.: *J. Soc. Chem. Ind.*, **64** (1945), p. 106.

(2) Chambers, E. G.: *Statistical Calculations for Beginners* (C.U.P., 1940).

(3) Baker, I. M., Dudding, B. P.: *J. Soc. Glass Tech.*, **17** (1933), p. 239.

(4) Dudding, B. P., Jennett, W. J.: *Quality Control Charts*, B.S. 600R (London, 1942).

(5) Jurkov, S.: *J. Tech. Phys.*, **1**, p. 386 (U.S.S.R., 1935).

(6) Morey, G. W.: *The Properties of Glass*, p. 320 (Reinhold, New York, 1938).

(7) Weibull, W.: *Ingeniörsvetenskapsakadamiens Handl.*, p. 149 (Stockholm, 1938).

(8) Poncelet, C. F.: *Metals and Technology* (April 1944), *Am. Inst. Min. and Met. Eng. Technical Publication*, p. 1684 (1944).

(9) Raman, C. V.: *Nature*, **103** (1919), p. 113.

(10) Preston, F. W.: *J. Soc. Glass Tech.*, **10** (1926), p. 236.

(11) Griffith, A. A.: *Phil. Trans. Roy. Soc.*, A 221 (1920), p. 163.

(12) Inglis, C. E.: *Proc. Inst. Naval Arch.* (May 1913).

(13) Littleton, J. T.: *Phys. Rev.*, **22** (1923), p. 510.

(14) Holland, A. J., Turner, W. E. S.: *J. Soc. Glass Tech. Trans.*, **20** (1936), p. 72.

(15) Timoshenko, S.: *The Theory of Plates and Shells*, pp. 76, 165 (McGraw Hill Book, 1940).

(16) Haward, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 5.
(17) Graf, O.: *Glastech. Ber.*, **13** (1935), p. 232.
(18) Mangler, W.: *Z. Phys.*, **93** (1935), p. 173.
(19) Jurkov, S.: *Phy. Z. Sowjet Union*, **1** (1932), p. 123.
(20) Preston, F. W.: *J. App. Phys.*, **13** (1942), p. 623.
(21) Boow, J., Turner, W. E. S.: *J. Soc. Glass Tech.*, **22** (1938), p. 357.
(22) Murgatroyd, J. B.: *J. Soc. Glass Tech.*, **28** (1944), p. 406.
(23) Andrade, E. N. da C., Tsien, L. G.: *Proc. Roy. Soc. A.*, **159** (1937), p. 346.
(24) Williams, A. E.: *J. Am. Ceram. Soc.*, **6** (1923), p. 980.
(25) Smekal, A.: *Glastech. Ber.*, **13** (1935), p. 141.
(26) Bailey, J.: *Glass Ind.* (Jan.–April 1939).
(27) Black, L. V.: *Bull. Am. Ceram. Soc.*, **15** (1936), p. 274.
(28) Gooding, E. J.: *J. Soc. Glass Tech.*, **16** (1932), p. 145.
(29) Murgatroyd, J. B.: *J. Soc. Glass Tech.*, **28** (1944), pp. 368, 388.
(30) Preston, F. W.: *Brit. Plast.*, **16** (1944), p. 440.
(31) Weibull, W.: *Ingeniörvetenskapsakad. Handl.*, **151** (Stockholm, 1939).
(32) Campbell, H. L.: *Proc. A.S.T.M.*, **37**—II (1936), p. 66.
(33) Tucker, J.: *Proc. A.S.T.M.*, **45** (1945), p. 961.
(34) Tippet: *Biometrika*, **17** (1925), p. 364.
(35) Tucker, J.: *Proc. A.S.T.M.*, **45** (1945), p. 953.
(36) Gehlhoff, G., Thomas, M.: *Z. Tech. Phys.*, **7** (1926), p. 105.
(37) Greene, C. H.: *J. Am. Ceram. Soc.*, **15** (1932), p. 59.
(38) Schott, O., Winkelman, A.: *Ann. d. Phys. und. Chem.*, **51** (1894), p. 697.
(39) Graf, O.: *Glastech. Ber.*, **7** (1929), p. 143.
(40) Preston, F. W.: *J. Am. Ceram. Soc.*, **18** (1935), p. 220.
(41) Holland, A. J., Turner, W. E. S.: *J. Soc. Glass Tech.*, **24** (1940), p. 46.
(42) McCormick: *Bull. Am. Ceram. Soc.*, **15** (1936), p. 268.
(43) Apelt, G.: *Z. Physik*, **91** (1934), p. 336.
(44) Harries, W.: *Z. Tech. Phys.*, **18** (1937), p. 48.
(45) Seddon, E.: *J. Soc. Glass Tech.*, **22** (1938), p. 268.
(46) Murgatroyd, J. B., Sykes, R. F.: *J. Soc. Glass Tech.*, **31** (1947), p. 17.
(47) Orowan, E.: *Nature*, **154** (1944), p. 341.
(48) Rehbinder, P.: *Nature*, **159** (1947), p. 866.
(49) Baker, T. C., Preston, F. W.: *J. App. Phys.*, **17** (1946), p. 162.
(50) Gough, H. J.: *J. Inst. Met.*, **49** (1932), p. 17.
(51) Gough, H. J., Sopwith, D. G.: *J. Inst. Met.*, **49** (1932), p. 93.
(52) Evans, U. R., Simnad, M. T.: *Proc. Roy. Soc. A.*, **188** (1947), p. 372.
(53) Haward, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 426.

(54) PRESTON, F. W.: *Nature*, **156** (1945), p. 55.

(55) GLATHART, J. R., PRESTON, F. W.: *J. App. Phys*, **17** *(1946), p. 189.*

(56) TAYLOR, N. W.: *J. Colloid Sci.*, **2** (1947), p. 185.

(57) MURGATROYD, J. B.: *Nature*, **154** (1944), p. 51.

(58) MURGATROYD, J. B., SYKES, R. F.: *Nature*, **156** (1945), p. 716.

(59) MURGATROYD, J. B., SYKES, R. F.: *J. Soc. Glass Tech.*, **31** (1947), p. 36.

(60) GURNEY, C.: *Nature*, **156** (1945), p. 306.

(61) SMEKAL, A.: *Naturwiss.*, **15** (1936), p. 106.

(62) MENGELKOCH, H.: *Z. Physik*, **97** (1935), p. 46.

(63) VONNEGUT, B., GLATHART, J. L.: *J. App. Phys.*, **17** (1946), p. 1082.

(64) JONES, G. O., TURNER, W. E. S.: *J. Soc. Glass Tech.*, **26** (1942), p. 35.

(65) SCHARDIN and STRUTH: *Glastech. Ber.*, **16** (1938), p. 219.

(66) EDGERTON, H. E., and BARSTOW, F. E.: *Glass Ind.*, **20** (1939), p. 174; *J. Am. Ceram. Soc.*, **24** (1941), p. 131; **22** (1939), p. 306.

(67) BAIRD, K. M.: *Nature*, **160** (1947), p. 24.

(68) MULLER, K. H.: *Z. Physik.*, **69** (1931), p. 431.

(69) WIRTZ, K.: *Z. Phys.*, **93** (1935), p. 292.

(70) SUZUKI, S.: *Proc. Phys. Math. Soc., Japan*, **3-4** (1921–2), p. 168.

(71) TRELOAR, L. R. G.: *Trans. Inst. Rubber Ind.*, **19** (1944), p. 201.

(72) LITTLETON, J. T., PRESTON, F. W.: *J. Soc. Glass Tech.*, **13** (1929), p. 336.

(73) HOLLAND, A. J., TURNER, W. E. S.: *J. Soc. Glass Tech.*, **19** (1935), p. 221.

(74) HAWARD, R. N.: *Nature*, **157** (1946), p. 21.

(75) VON REIS, L.: *Glastech. Ber.*, **13** (1935), pp. 239–43.

(76) PRESTON, F. W.: *J. Am. Ceram. Soc.*, **16** (1933), p. 163.

(77) WINKELMAN, A., SCHOTT, O. : *Ann. d. Phys. und. Chem.*, **51** (1894), p. 697.

CHAPTER IV

THE DEFORMATION OF PLASTICS AND GLASS

THIS chapter is concerned with the manner in which glasses and plastic materials are deformed, more particularly within the temperature ranges in which they are normally employed. For this reason no discussion is given of the many phenomena which occur at or near the melting point of glass. Rather the intention is to use glass as an example of a material which accurately obeys Hooke's law of deformation and which may therefore be treated as an "ideal" elastic solid.[1] Similarly it is not intended to deal at length with the flow of plastics at high temperatures though this is of great technical importance in connection with the operations of moulding and extrusion. Instead it is simply noted that plastics are, in varying degree, unsuitable materials where high temperatures are concerned.

For some time it has been widely recognized both in theory and practice that the deformation of various materials was not all of one type. Gurevich,[2] and Alexandrov and Lazurkin[3] divided the deformation D of plastic materials into ordinary D_{OF}, highly elastic D_{HE}, and viscous D_{visc} types. These divisions generally correspond with those put forward by the British Rheologists' Club[4] who noted three types of deformation with different materials, namely:

(1) Ideal elastic deformation which may or may not be Hookean (i.e. proportional to the stress). This takes place immediately a stress is applied and disappears when the stress is removed.

(2) Non-ideal elastic deformation which develops slowly after the application of the stress and is ultimately recoverable.

(3) Various sorts of viscous flow all of which have the property of not being recoverable and involving a permanent change in the material.

Again, with high molecular compounds, these three types of deformation are commonly related to the three molecular mechanisms of the deformation of primary bonds D_{OE}, chain uncoiling D_{HE}, and chain slipping D_{visc} (Fig. 25). Nevertheless these definitions do not always completely correspond, the most important cause of discrepancy being due to the wide range of time factors involved in the highly elastic deformation. Thus the deformation of rubber, which molecularly is of the highly elastic type, may be classified as an ideal elastic deformation by the rheologist since the time element is small. On the other hand, a deformation sometimes does not appear to be a reversible one, but when the material is warmed or treated with a swelling agent it becomes reversible. In this book both these deformations will be classed as highly elastic, that is to say the term ultimately recoverable is interpreted to include forms of treatment calculated to assist recovery, and the deformation of rubber is looked upon as similar to other types of deformation, depending on the same molecular mechanism, even though the time factors involved with rubber may be small or even negligible.

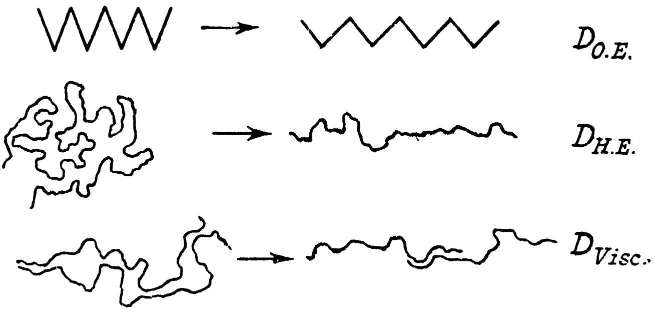


FIG. 25.—A diagrammatic illustration of the various types of deformation in plastic materials.[37]

The justification for this separation of the different types of deformation in plastic materials is supported by evidence from other sources. For instance, McNally and Sheppard[5] showed that the ideal elastic deformation of cellulose ester films took place with an absorption of heat, but that at the "yield point" (i.e. where D_{HE} and perhaps D_{visc} occur) the deformation process is accompanied by the emission of heat. Similarly a rough correspondence exists between the volume-temperature curve of a plastic as ordinarily measured, and the onset of high elasticity. If a plastic which is capable of the highly elastic type of deformation is cooled down a temperature range is reached below which the material will break before any highly elastic deformation can be brought about. At such temperatures the large deformations characteristic of high elasticity may be entirely suppressed. By making measurements of the change in volume of different polymers with temperature Ueberreiter[6] demonstrated that a discontinuity occurred in the volume-temperature relation and this has been shown to occur in the same temperature range as that in which this high elasticity is first developed, and measurements of this transition point are often quoted. For an example of a curve of this type, see Fig. 39. The essential feature of these measurements is that both the changes in the volume-temperature curve and the onset of high elasticity are assumed to be controlled by the same molecular process, namely the occurrence of free rotation in the molecular chains. In one sense there can be no doubt that a fundamental change takes place at the observed transition point since at one temperature it can be said that substantially no rotation of molecular bonds occurs, but at a higher temperature rotation takes place readily and largely determines the properties of the material. However, certain difficulties arose in a detailed investigation carried out with polystyrene; Boyer and Spencer[7] showed that the precise temperature at which a change in slope of the volume-temperature curve is observed depended on the rate of heating. They also found that if the polymer was heated up to any particular temperature there follows a steady isothermal change in volume, so that the specific gravity tends to a particular value characteristic of the temperature. They regarded this as the true equilibrium specific gravity of the material at the temperature concerned; when it is plotted against temperature they obtain the curve (*a*) shown in Fig. 26. This so-called equilibrium curve shows no transition point. Boyer and Spencer also investigated the rates at which the volume of the plastic changes towards the equilibrium value at different temperatures, and were able to estimate the activation energy involved in the process of adjustment; this is 12,000 cal. as compared with 61,000 cal. for highly elastic recovery. They therefore concluded that the apparent transition point in the volume-temperature curve, as ordinarily measured, does not depend on the same molecular processes as the development of high elasticity, although it does reflect the increased ease of molecular adjustment which occurs at approximately the same time.

In these circumstances the status of the conception of a true thermodynamic transition point, measurable from the volume-temperature curve, must depend much on the views held of the value and probable generality of Boyer and Spencer's results. However, there is not much evidence at present available with other plastics; though there can be little doubt that in the temperature range where high elasticity sets in there is a fundamental change in the internal condition of the material. Further evidence comes from the work of Fuoss,[8] who found that several plastic materials show a marked change in their electrical properties in the same temperature range as that in which the alteration in their mechanical properties occurs, a result entirely in accordance with the theory of free rotation above a transition point.

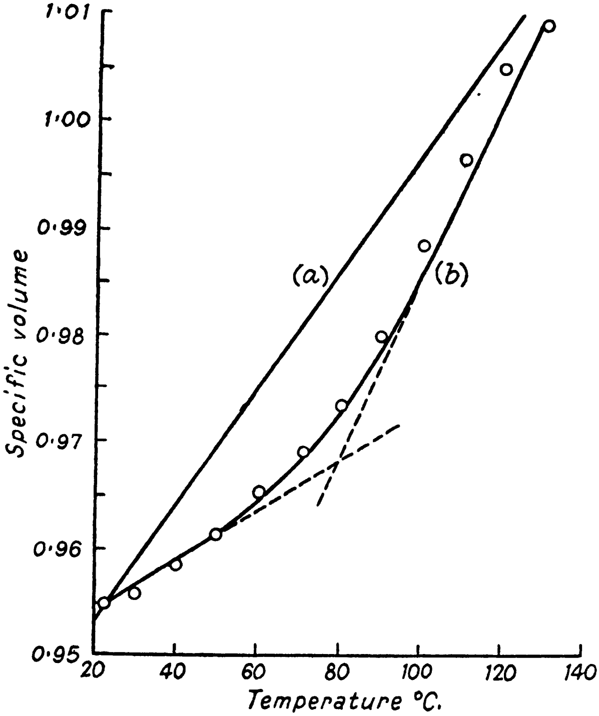


FIG. 26.—Volume changes in polystyrene at different temperatures. The line (*a*) represents the estimated volume at equilibrium and curve, (*b*) that normally measured in a simple heating experiment. The intersection of dotted lines is the transition temperature.[7]

The Ordinary Elastic or Ideal Hookean Deformation

For most purposes the ordinary elastic deformation of plastics may be treated as having no time factor; however, this does not mean there are no limitations upon this mode of deformation arising from high rates of application of stress. Actually such a limitation necessarily arises because any deformation implies motion in a material having mass. However, in most deformation experiments the velocity of deformation is such that neither the forces involved in moving the material, nor the consequences of the limited rate of propagation of stress waves, are of much significance, but these forces can and do become significant under conditions of high velocity impact. This, then, is the limitation involved when the ordinary elastic deformation is described as ideal, i.e. occurring immediately upon application of the stress. But the extent to which most ordinary elastic deformations are to be described as Hookean, i.e. proportional to the stress over all stress ranges, is less clear, since at high stresses most plastic materials show much larger deformations of other types, which effectively mask any quantitative discrepancies which might occur in the ordinary elastic deformation. Massive glass exhibits the ordinary elastic deformation, and the degree of the effect is generally taken to be proportional to the stress; attempts to discover slow deformations not proportional to the stress at normal temperatures have proved difficult to carry out, and lead to controversial results. In any case the deviations from ideal Hookean behaviour are certainly small. On the whole, therefore, the assumption that plastics show a similar ideal elastic deformation, strictly Hookean in character, seems reasonable pending the accumulation of evidence to the contrary.

Isotropic materials which show the ordinary elastic deformation exclusively or predominantly will obey the classical relations of elasticity, provided the deformations are small, as is usual in such cases. Thus if Young's modulus E or Poisson's ration σ are determined the other moduli will be given by the relations

$$\left.\begin{aligned}\text{Shear modulus} &= G = \frac{E}{2(1+\sigma)}\\ \text{Bulk modulus} &= K = \frac{E}{3(1-2\sigma)}\end{aligned}\right\}\ \text{for isotropic materials.}$$

The Deformation of Glass

Deformation of massive glass at ordinary temperatures is almost entirely of the ideal Hookean type. For instance a recent paper describes delayed elastic effects amounting to 1 per cent or less of the ideal Hookean deformation.[9] Its properties are therefore capable of description by any two of the elastic constants. Three of these constants, the compressibility, Poisson's ratio, and the Young's modulus, have been the subject of much experimental work, but only the last two will be dealt with here as they enter most directly into strength relations. A summary of the work on compressibility is given in Morey.[10]

Poisson's ratio σ has been measured by Auerbach[11] by means of indentation experiments and values of 0·17 to 0·30 were obtained with a series of glasses. Although there is no doubt about the approximate correctness of these results, they are not in exact agreement with those of Straubel (see Chap. V). Straubel,[12] who made experiments on similar glasses to those used by Auerbach, used a more direct method of measurement. A glass beam was bent in an arc and the longitudinal and transverse curvatures were observed by means of the locations of interference fringes. From his results he constructed a list from which the Poisson's ratio of any glass could be calculated by multiplying the appropriate figure by the molar proportions by weight of the various constituents. The results are claimed to be accurate to within 0·01. The figures are as follows:

SiO_2	0·1533	B_2O_3	0·2840	ZnO	0·3460	PbO	0·2760
Al_2O_3	0·1750	BaO	0·3560	Na_2O	0·4310	K_2O	0·3969
CaO	0·4163	P_2O_5	0·2147	Sb_2O_3	0·2772	MgO,As_2O_5, Mn_2O_3	0·2500

Thus a soda-lime-silica glass of composition[13] 73 per cent SiO_2, 2 per cent Al_2O_3, 9 per cent CaO, 3 per cent MgO, 13 per cent Na_2O would have a value of $\sigma = 0·22$.

A great number of measurements of the Young's modulus of elasticity have been carried out. One of the first methods applied was that of measuring the angle through which the ends of a loaded beam were deflected by means of a suitable arrangement of mirrors and a light source.[14, 15] Subsequently measurements have been made directly on the bending of glass beams[16, 17] and on the vibration of long beams in the horizontal plane.[18] So far, no definite differences have emerged between measurements made statically and dynamically; slow vibration and bending experiments[18] have given identical results within the experimental error.

Further, determinations of the velocity of sound in silica glass by Ide[19] gave values of $E = 740{,}000$ kg./cm.^{2} comparing with a figure of 720,000 kg./cm.^{2} given by Sosman[20] for other methods. Finally Bhagavantam and Rao[21] have confirmed the independence of the elastic modulus from time effects for all practical purposes by comparing the results obtained with a supersonic wave technique and by static methods. They found values of 490,000 and 470,000 kg./cm.^{2} respectively by the two methods.

Among the many static measurements of the Young's modulus, the early work of Winkelman[15] gave values of 500–800,000 kg./cm.^{2} for a series of glasses of differing composition and these results are still generally accepted. A more systematic series of measurements are recorded in the paper by Gehlhoff and Thomas[22] on the variation in mechanical properties with composition. Most of their results lay between 600–800,000 kg./cm.,^{2} but by replacing SiO_2 by CaO in an 82 per cent SiO_2 18 per cent Na_2O glass a modulus of 1,000,000 kg./cm.^{2} could be reached with 20 per cent CaO. In general, there is a marked contrast between the comparative ease with which measurements of the elasticity of glass have been carried out and the difficulties encountered in any strength determination involving rupture, and this distinction is to be explained by the fact that elasticity is a true bulk property of the glass, independent of the occurrence of adventitious flaws.

The *variation* of the Young's modulus of elasticity of glass with *temperature* has been variously reported and appears to depend on the type of glass used. In all cases it may be assumed that changes are small in the range of 0 to 100° C. and may consequently be neglected for most strength purposes. This relative constancy for a soda-lime-silica glass is illustrated in Fig. 27, taken from the work of Jones,[23] and it will be seen that the modulus is extremely constant below 300° C. On the other hand Winkelman[15] and other workers[24, 16] have found small but definite declines in Young's modulus with increasing temperature. It would be tempting to ascribe some of these results to the occurrence of small delayed elastic effects (which were separately investigated in Jones's experiments), but the fact that Ide obtained a similar decline, using his sound velocity technique, seems to make this explanation most unlikely. Moreover, with silica and Pyrex glass Ide found a slight *increase* in the modulus with rising temperature, and the result is supported by the work of Lees *et al.*,[17] although the absolute values of the elastic moduli varied rather curiously in their experiments according to the previous treatment of the silica rod. Further, declines in compressibility of silica and Pyrex glass with increasing temperature have been reported by Birch and Dow[25] as opposed to a soda-lime glass where the compressibility rose steadily with increasing temperature. It must therefore be concluded that glasses do not behave uniformly with regard to the small changes in the moduli of elasticity with increasing temperature below the softening point, and that the nature of the variation depends on the composition.

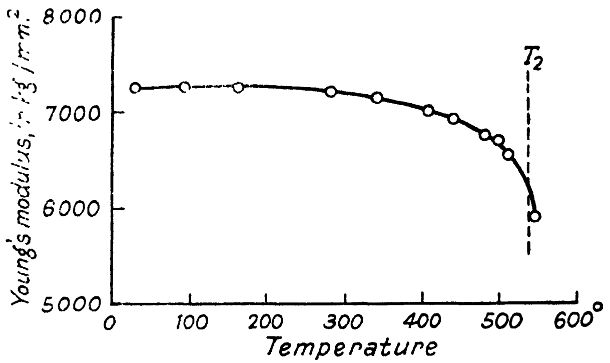


FIG. 27.—The variation of the Young's Modulus of a soda-lime-silica glass with temperature.[23]

At higher temperatures there is full agreement that glass shows both delayed elastic and viscous deformations somewhat similar to those given by plastic materials. The deformation of glass at temperatures above 400° C. has been investigated by Taylor.[26] For his soda-lime-silica glass, Jones[23] found that the delayed elastic effect rose from 3 per cent of the instantaneous deformation at 200° C. to 75 per cent at 444° C., and it again follows from these results that slow deformations may be comfortably neglected at room temperatures.

However, this conclusion does not apply to glass fibres, which do show small delayed elastic, and possibly viscous, deformations when subject to stress at ordinary temperatures. These properties were the subject of a number of early investigations by Kohlrausch *et al.*, whose results have been summarized in a recent monograph.[27] There is controversy on the magnitude of the elastic modulus obtained with glass fibres, which is normally still dominated by the reversible Hookean effect. Firstly, the investigations of Jurkov[28] gave results in which the elasticity was *independent* of the fibre diameter using glass and quartz fibres in the range 0 to 100 μ. More recently Murgatroyd,[29] in a series of bending experiments, found that the elastic modulus decreased as the diameter of the fibre was reduced; he reports that a fall in the Young's modulus from 700,000 to 450,000 kg./cm.^{2} takes place as the fibre diameter is reduced from 0·1 to 0·002 cm. Finally Slayter,[30] making measurements in tension (Plate XVI), found that fibres of 0·00070 to 0·00020 in. diameter have a constant elastic modulus of 8,000,000 to 9,000,000 lb./in.,^{2} while with still thinner threads the modulus tends to *rise*. Obviously, not very much can be concluded from these results, but further measurements, both in bending and tension, would be of value for a particular group of glass fibres.

Ordinary Elastic Deformation of Plastic Materials

It is generally supposed that the existence of an ideal Hookean or ordinary elasticity in plastic materials is due to the separation of molecular chains and/or the deformation of co-valent links under the action of the stress without the intervention of steps involving substantial molecular rearrangement. The detailed account of these processes has been worked out in a number of different ways, and slightly differing results obtained according to the model chosen or the treatment devised. Some of these calculations of the Young's modulus of elasticity are summarized in Table XIII.

In this case it is clear that the divergence between theory and

TABLE XIII. CALCULATED AND MEASURED VALUES OF THE YOUNG'S MODULUS OF HOOKEAN ELASTICITY

Author	Method	Result	Experimental figures
Kuhn[31] ..	Chain separation	10^4—10^6 kg./cm.^{2}	In agreement with many hard plastics
de Boer[32] ..	Chain separation	$1·1 \times 10^6$ kg./cm.^{2}	1—0·8 10^5 for phenol-formaldehyde[34]
Meyer and Lotmar[33]	Elastic forces of C—C and C—O bonds in *oriented* cellulose	0·79—$1·23 \times 10^6$ kg./cm.^{2}	0·5—$1·1 \times 10^6$ kg./cm.^{2} dry oriented cellulose fibres[33]

experiment is smaller than is the case with strength calculations, and the agreement may be ascribed to the characteristic that elasticity is a bulk property of the material. Nevertheless, on the whole, the calculations give results which correspond to the highest figures obtained under experimental conditions and other factors may reduce elasticity. For instance, Meyer and Lotmar note that wet ramie fibre has a lower modulus of elasticity than the dry material, while numerous other experiments have shown that the effect of plasticizers is to give a lower value of the modulus of elasticity. Some doubt exists whether the reduction of elastic modulus occurring in such conditions, or with a rising temperature, really consists of a change in the true Hookean modulus. There is always a possibility that the variation may actually be brought about by a decrease in the time factor of some intrinsically non-ideal elastic effect; but here the elastic modulus would be expected to depend on frequency at short times, and, since examples of a modulus changing with temperature but not with frequency have been established, it seems reasonable to accept other reported variations in elastic modulus as partly due to genuine changes in Hookean elasticity. However, this analogy does not appear to apply to very soft materials, where separation of the elastic effects may become difficult or even impossible.

TABLE XIV. EFFECT OF PLASTICIZERS IN THE ELASTICITY AND IMPACT STRENGTH OF CELLULOSE ACETATE[35]

	Modulus of elasticity	Charpy impact strength
	lb /in ²	ft -lb /in ²
Dimethyl phthalate		
28%	529,000	3·4
31%	468,000	4·0
34%	364,000	4·7
o- and p-toluene sulphonamide (mixture)		
28%	708,000	2·9
31%	653,000	2·1
34%	552,000	1·4

Typical measurements of variation of Young's modulus with plasticizer content have been given by Gloor,[35] who derived his values from the tangent at the origin of the stress-deformation curve obtained by deforming stiff materials ($E > 140{,}000$ lb./ft.^{2} = 10,000 kg./cm.^{2}) under light loads.[36] For instance, in a typical series of experiments, he gives the following figures for the effects of dimethyl phthalate and *o*- and *p*-toluene sulphonamide plasticizers on cellulose acetate (53 per cent acetic acid) at 70° F. and 60 per cent humidity (Table XIV).

As already stated, rise in temperature generally causes a reduction in the Young's modulus of elasticity, though the effects are less pronounced than in other types of elastic behaviour.[37] For instance, Bartoe[38] has given curves for the deformation of an acrylic type resin which show that the slope of the initial part of the stress-strain curve, where the relation is linear and the deformation probably all of the ideal Hookean type, is temperature-dependent, and a similar decline in the modulus of elasticity has been reported for "Perspex" methacrylate sheet.[39] Gloor[35] has also given figures for the effect of temperature on elastic modulus as shown in Fig. 28, which illustrates the characteristic decline. Other experiments, in which precautions were taken to exclude deformations not immediately reversed on removal of the load, are reported by Rohs and Hauck.[40] They record changes in elastic modulus for phenol formaldehyde, urea formaldehyde, polymethyl methacrylate, and polyvinyl chloride, which all decrease with increasing temperature and are generally similar to those reported by Gloor. In the case of experiments at high frequencies, measurements of the temperature variation of Young's modulus in the range of 40,000 to 70,000 sec.$^{-1}$ where the elasticity was independent of the frequency have been carried out by Rinehart[41]

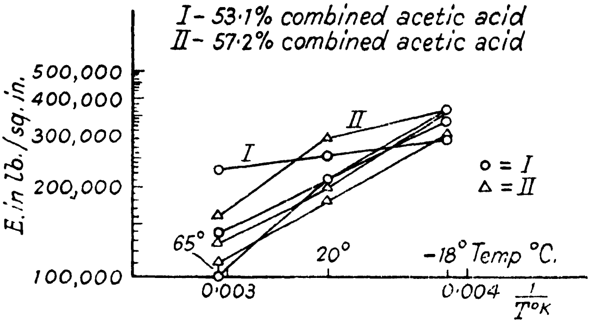


FIG. 28.—The effect of temperature on the approximate Hookean elastic modulus of plasticized cellulose acetate.[35]

on Lucite (acrylic) and Karolith (Casein) plastics. In each case, plots of $1/E$ against temperature were linear at low temperatures, but became curved as temperatures were approached where non-ideal elastic effects became appreciable. The results (Table XV) illustrate the degree of change in the ideal Hookean elasticity with rising temperature as measured by an experimental method which reduces the contributions of delayed elastic effects to a minimum.

TABLE XV. EFFECT OF TEMPERATURE ON THE HOOKEAN MODULUS OF TWO PLASTICS MEASURED AT HIGH FREQUENCIES[41]

Lucite (polymethyl methacrylate)		Karolith (casein plastic)	
Temperature	Young's modulus	Temperature	Young's modulus
°C	kg/cm ^{2}	C	kg/cm ^{2}
− 55	67,000	25	63,000
0	53,500	75	52,000
26	48,000	110	43,000
61	39,000		

A comparison with static measurements was not made in this paper, but Press and Mark[42] have measured both the dynamic (10^{-3}–10^{-4} sec.) and a short time (10^{-1}–10^{-2} sec.) moduli for viscose and acetate rayon fibres and found only small differences between the two (Table XVI).

TABLE XVI. DYNAMIC MODULI OF VISCOSE RAYON

Material	Dynamic modulus in 10^{10} dyne/cm ^{2} Time, 10^{-3}–10^{-4} sec	Short time modulus in 10^{10} dyne/cm ^{2} 10^{-1}–10^{-2} sec
Viscose rayon, before any stretching ..	15	10
Viscose rayon at 0·75% elongation ..	17	15
Viscose rayon at 4% elongation .. .	20	20
Viscose rayon at 60% of elongation to break	50	45

The independence of elastic modulus and frequency of plasticized polyvinyl chloride at frequencies of 80 to 1,400 sec.$^{-1}$ has been reported by Sack, Motz and Work,[43] and they also found that elastic modulus decreased with temperature. However, in another paper[44] they reported that the same material showed a decrease by a factor of 4 to 10 in the elastic modulus when this was measured under static conditions. Similarly Eley and Pepper[45] found that as the time of measurement was reduced from several minutes down to 10 sec. the elastic modulus of a very soft plasticized cellulose derivative steadily increased.

The author's experience suggests that a hard celluloid ($E = 17{,}000$ kg./cm.^{2}) gave a definite and easily measurable reversible Hookean modulus, but that with a softer plasticized cellulose acetate ($E = 2{,}400$ kg./cm.^{2}) it was not easy to eliminate slow elastic effects entirely, even with the smallest stresses used. On the whole it may therefore be concluded that as materials become softer it becomes increasingly difficult to separate the various elastic effects and that the larger non-ideal deformations more and more tend to obscure the truly Hookean effects. Nevertheless, on the balance of evidence, the decline in the Hookean modulus with increase in temperature and plasticizer content seems a genuine effect, to be considered in evaluating the mechanical properties of simple plastics.

The effect of molecular weight on elastic properties may be observed in Table II; elasticity is notably less sensitive in this respect than strength measurements. It seems probable that in this case the deformations were mainly of the ideal Hookean type.

The Non-ideal Deformation of Plastic Materials

If we now return to our original proposition concerning the deformation of plastics we can write, assuming the Boltzmann theory of the independent superposition of deformation:

$$D = \text{total deformation} = D_{OE} + D_{HE} + D_{visc}$$

$$\frac{S}{E} + D_{HE} + D_{visc} \quad \text{(in tension)}$$

Those sorts of deformation which fall under the heading of D_{HE} are ascribed to the uncoiling and rearrangement of molecular chains. In accordance with theory we find that large non-ideal elastic deformations of 50 per cent or more are confined to the thermoplastic materials and are not normally shown by the highly cross-linked phenolic resins. Nevertheless, these deformations are not suppressed by a moderate degree of cross-linkage (rubber), though they are gradually eliminated if the amount of cross-links is increased (ebonite). The theory of chain rearrangement is supported by the observation that the highly elastic deformation takes place largely without change of volume (Poisson's ratio 0·5), and so fresh relations apply between elastic constants not developed in classical elasticity theory. For example, Treloar[46] has shown that a pure shear can be applied by stretching a wide sheet of rubber, so that in one direction extension takes place, in another retraction, and the third dimension remains unaltered. This procedure, which relates behaviour in shear to materials showing large deformations, does not apply where $\nu \neq 0 \cdot 5$.

Although it is not intended to discuss in detail the deformation properties of rubber, it must be recognized that much of the present theory of the highly elastic deformation of plastics is founded upon theories embodying equilibrium relationships which were first applied to rubber, and an account of these theories must be included. The kinetic theory of elasticity as applied to rubber was first clearly expressed by Meyer *et al.*,[47] and developed mathematically by Kuhn,[48] and Guth and Mark.[49] Essentially rubber is held to consist of long chain molecules whose length from end to end is determined by probability factors derived from the consideration of all the possible configurations of a long molecular chain. In this way distance between the two ends of such a chain is expressed by the following relation:

$$p(r)\,dr = \frac{4\beta^3}{\pi^{\frac{1}{2}}} r^2 e^{-\beta^2 r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $p(r)$ is the probability of a length of between r and $r + dr$, and in the particular case of a paraffin chain β is given by the relation,

$$\frac{1}{\beta^2} = \frac{2}{3} l_c^2 Z \frac{1 + \cos\theta}{1 - \cos\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

here l_c is the length between freely-rotating links (the c–c bond distance for a paraffin chain), Z the total number of links and θ the valency angle. The curve from relation (1) as plotted by Treloar[50] is shown in Fig. 29. Appropriate thermodynamic treatment of the above relations, in which entropy is introduced as the logarithm of the probability, shows that the stress in a piece of extended rubber should be proportional to the absolute temperature. In general, it has been found that the tension in extended rubber does increase as the temperature is raised (in contrast to the behaviour of metals and most Hookean solids), and in certain experiments by Meyer and Ferri[51] a good linearity with temperature was obtained (Fig. 30). This work has recently been extended.[52] An essential element in the equilibrium theory of high elasticity is that the long rubber molecules are not extended to anything approaching their full length, in which case the relations

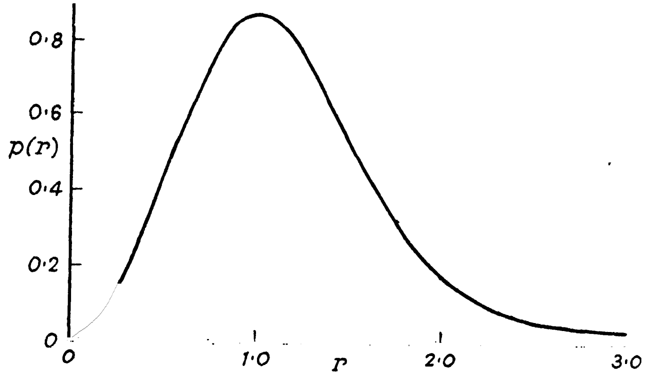


FIG. 29.—The form of the distribution curve for the probability of the separation of the ends of a long paraffin chain.[50]

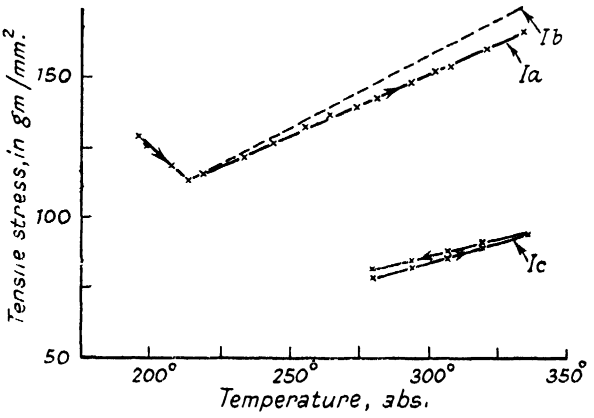


FIG. 30.—The observed tension in stretched rubber plotted against the absolute temperature.[51]

of Kuhn do not apply in the same form; Treloar[46] showed that the stresses increase markedly above those predicted by the simple theory at high extensions, and also[50] by a slight modification of the principles enunciated by Busse[53] he summarized the main conditions for high elasticity as follows:

(1) The presence of long chain molecules possessing freely rotating links.

(2) Weak secondary forces between the molecules.

(3) An interlocking of the molecules at a few places along their length to give a three dimensional "network."

The last of these three has been the basis of a further development in the theory of the deformation of rubber undertaken by Wall,[54] and by James and Guth,[55] who calculated the probability of a deformation α under tension or compression, where $\alpha = l/l_0$ and the original length l_0 has been extended (or compressed) to l.

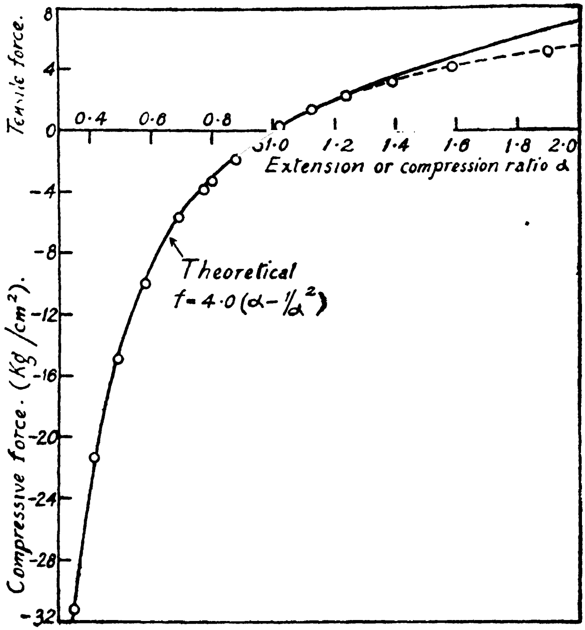


FIG. 31.—The theoretical and experimental equilibrium behaviour of rubber under tension and compression for small or moderate deformations.[46]

He then used this relation in a formula for the tension S of a cylinder of original cross-section 1 cm.,^{2} namely:

$$S = \rho \frac{RT}{M}\left(\alpha - \frac{1}{\alpha^2}\right)$$

where M is the molecular weight between points of interlocking and ρ the density.

Treloar[46] has also shown that provided the deformations are not too large a relation of this form can successfully account for the experimental results under tension and compression in a single curve (Fig. 31). The deviation between experiment and theory shown in this curve at the highest tensions is in the opposite sense and on a much lesser scale than those deviations which take place at elongations of 600 to 700 per cent where the stress rises to more than double the predicted value (Fig. 32, curve (*a*)).

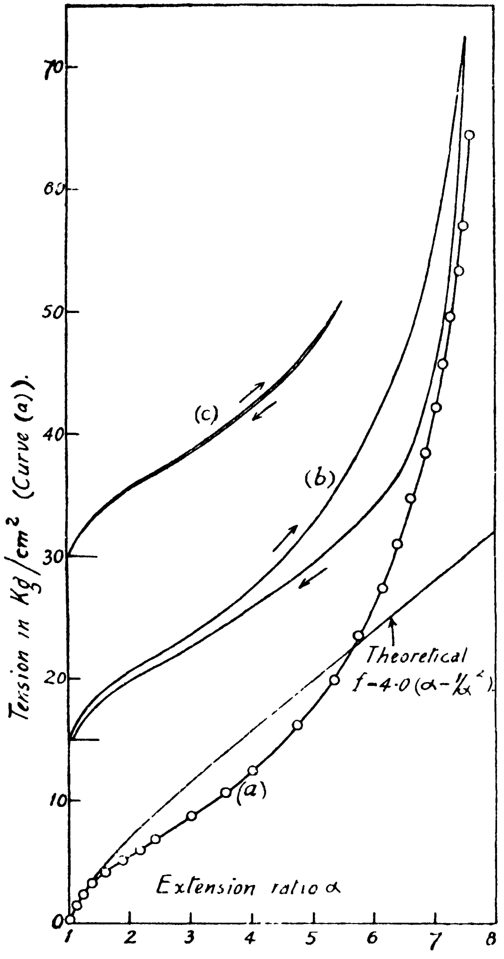


FIG. 32.—Large extensions in rubber. The displaced curves indicate the hysteresis effects after different deformations.[46]

All these theories neglect the effect of possible loose ends or terminal chains connected to the network by one end only, but a consideration of this has recently been made the basis of an important theoretical development by Flory.[56] He investigated the

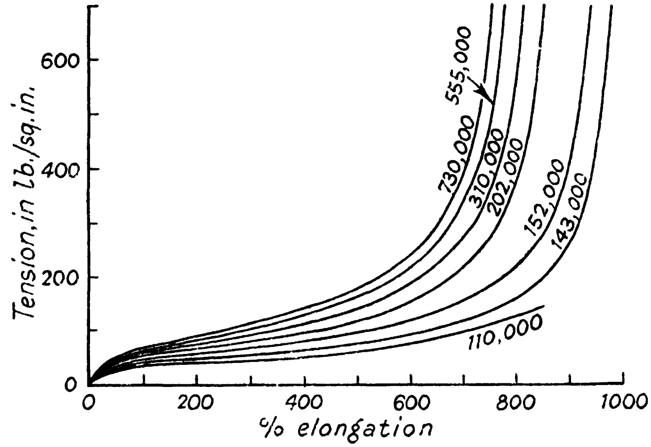


FIG. 33.—The stress-elongation curves for slightly vulcanized Butyl rubbers of differing initial molecular weight.[56]

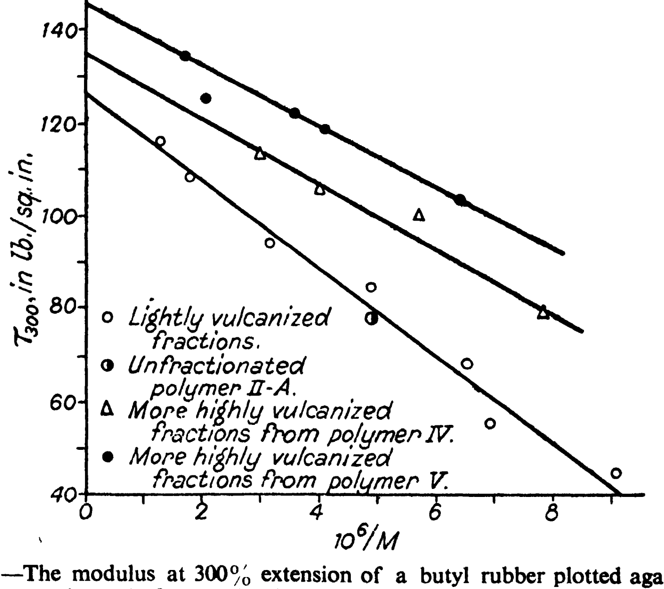


FIG. 34.—The modulus at 300% extension of a butyl rubber plotted against the reciprocal of the molecular weight before vulcanization.[56]

effect of the molecular weight of the initial polymer on the mechanical behaviour of a slightly vulcanized butyl rubber. Resulting stress-strain curves (Fig. 33) show clearly how the stress required to cause a given deformation is increased as the molecular weight of the original polymer is raised. Similarly, the deformations at which the curve becomes nearly vertical are reduced. These curves may be further elucidated by plotting the "modulus" at 300 per cent elongation against $1/M$, where M is the number average molecular weight of the polymer before vulcanization (Fig. 34). It is seen that a reciprocal relation between molecular weight and elastic "modulus" is clearly indicated. It seems probable that there will also be a tendency for the observed "modulus" to decrease as the molecular weight is raised with most polymers, showing the highly elastic type of deformation.

Effect of Temperature on High Elasticity—Mechanical Measurements

The above theory deals with equilibrium deformation in rubbers at temperatures where the tension is determined by the tendency for the molecules to return to their most probable configurations. Under these conditions as the temperature is raised the stress at a given deformation increases, since it is the thermal agitation which tends to favour purely random configurations and so to bring back the rubber to its normal shape. However, if the temperature of a rubbery material is steadily reduced the frictional forces tending to oppose the intermolecular rearrangements, which are necessary for equilibrium deformations to be reached, increase. So energy comes to be absorbed in the process of molecular rearrangement and the stresses arising therefrom may grow to be larger than those which derive from the true forces of high elasticity. At still lower temperatures the internal forces of friction may become so large that the stresses required to bring about the rearrangement necessary for showing a high elastic deformation are well above the breaking strength of the material, and the "rubber" behaves like a glassy Hookean solid. Between the extremes of the "glassy" and "rubbery" states there exists, for materials capable of true high elasticity, a region where deformation is markedly dependent on the time. This was clearly demonstrated for methacrylate polymers by Alexandrov and Lazurkin.[3]

Recently some interesting curves for a butadiene-acrylonitrile synthetic rubber have been obtained by Conant and Liska,[57] who measured an elastic modulus in bending after specific times and over a range of temperatures (Fig. 35). The results show that time effects are small at 0° C. and — 60° C. but that in between these limits is a marked separation of the curves based upon different

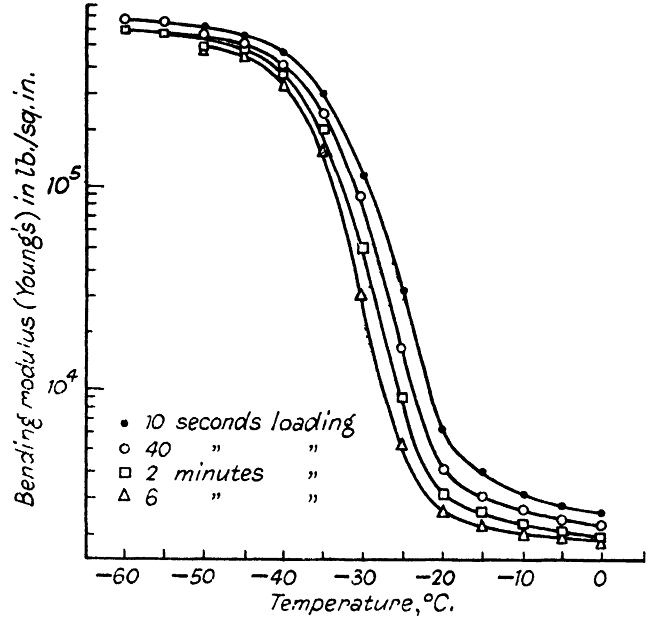


FIG. 35.—The elastic modulus of a butadrene-acrylonitrile rubber for different temperatures and times of measurement.[57]

times of measurement. Over the whole temperature range the elastic modulus falls by a factor of 100, a difference which illustrates the great increase in deformability taking place as true high elasticity comes into play. Such changes in elastic modulus occur for most polymeric materials, though the temperature range at which the change comes about differs greatly for different substances, which can be characterized by this temperature or transition point. However, since the high elasticity of a material is not capable of representation by a single modulus, and because time and stress effects play a large part, the conception of an elastic temperature above which true high elasticity occurs has not yet been precisely defined, though the elasticity changes are generally so steep over the critical range that differences occasioned by variations in method of measurement are not large. Approximate data, together with a discussion of this subject, have been given by Tuckett[58] (Table XVII).

Tuckett concludes that the effects may be qualitatively explained through the ease of occurrence of free rotation along the molecular chains. Where bulky side groups occur, and particularly where all the carbon atoms along the chain are substituted, free rotation is commonly reduced. For instance, rotation is comparatively easy with polymethyl acrylate, but where a hydrogen is replaced by methyl as in polymethyl methacrylate the ease of rotation is greatly diminished and the elastic temperature raised. Where rings occur, as in polyvinyl formal, rotation is partially suppressed and the elastic temperature further increased. However, this effect is not universal; where the side groups take the form of paraffin chains particularly, the opposite occurs and the substituent groups make the material softer. In Chapter II this question was discussed in connection with the static strength properties of butyl methacrylate and various substituted cellulose esters, and it may be assumed that in these cases strength and deformation properties are roughly parallel. Certain copolymers, e.g. butadiene-styrene, where monomers tending to give hard and soft polymers are combined, need a comparatively large amount of the more rigid monomer to raise the elastic temperature since the tendency to restrict rotation is proportional to the square of the fraction of substituent groups.[59] For instance, with a 2 : 1 styrene-butadiene copolymer the transition temperature measured by the method of Ueberreiter,[60] i.e. from the volume-temperature curve,

TABLE XVII. TEMPERATURE OF ELASTIC TRANSITION FOR VARIOUS MATERIALS

Polymer unit	Transition temperature
	°C.
Isoprene (rubber)	– 50 to – 70
Chloroprene	– 50 to – 70
Isobutene	– 50 to – 70
Vinyl acetate	35 to 45
Methyl acrylate	20
Methyl methacrylate	70 to 90
Styrene	70 to 90
Vinyl chloride	100 to 110
Vinyl formal	115

comes to — 70° C. in spite of the high proportion of styrene present.

It has further been shown that the elastic transition temperature can be reduced by the addition of plasticizer. This shows that chain-chain interaction as well as rotation must play a part in these highly elastic effects. By applying alternating stresses to plasticized methacrylate polymers Alexandrov and Lazurkin[3] found that the deformation obtained depended on the temperature and the frequency of the applied stress; on the basis of a specific frequency factor, Tuckett[58] used their results, and also those of Miller, Busse and Davies,[61] to derive the elastic temperatures of plastic materials containing different quantities of plasticizer (Table XVIII), and thus to demonstrate the lowering of elastic temperatures to be obtained with suitable plasticizers.

TABLE XVIII. EFFECT OF PLASTICIZERS ON THE TEMPERATURE OF ELASTIC TRANSITION

System	Plasticizer	Elastic temperature
	%	C
Polymethyl methacrylate ..	0	125
	10	87
	30	56
Polyvinyl chloride	0	89
Tricresyl phosphate	10	70
	20	54
	30	32
	40	17
	50	− 10

The difference between the value given here for unplasticized methacrylate and that given in Table XVII is to be ascribed to differing experimental criteria, and illustrates the approximate nature of these temperatures in relation to mechanical properties. Tuckett[58] shows, too, that the temperature region of high elasticity is raised by cross-linking agents, and figures are given for vulcanized rubber and divinyl benzene-styrene copolymers which illustrate this type of behaviour.

Time Effect in Retarded Elasticity

It has been established that complex effects occur in the temperature region where high elasticity first comes into play. The description and explanation of these phenomena, which are in some degree characteristic of many of the ordinary plastic materials at the temperatures at which they are used, has been the subject of much theoretical and experimental work but has not yet reached a satisfactory stage. To explain the effects observed Burgers[62] put forward a number of models based on arrangements of elastic and viscous elements in series and parallel. One of his most widely applied models (Fig. 36) is the appropriate model for an equation quoted by Mark[63] and Tuckett:[37]

$$D = D_{OE} + D_{HE} + D_{visc}$$
$$= \frac{S}{E} + \frac{S}{E_{HE}}(1 - e^{-t/\tau}) + \frac{S}{\eta}t$$

where τ is a constant commonly known as the relaxation time (not the entity defined by Maxwell; the terms orientation and retardation time have been suggested[46]) and E_{HE} and η are moduli dependent on the highly elastic deformation and viscosity respectively. This equation has the advantage that a definite meaning can be given to τ if formulated as a rate constant, with a specific energy of activation describing its temperature dependence, but it has two disadvantages. Firstly, the highly elastic deformation cannot be regarded as proportional to the stress even in equilibrium theory, since this is not so with rubber,[64] and with many plastic materials departures from stress proportionality may be large. Secondly, the existence of the viscosity term, which is assumed to be linear with time, has led many workers to assume that the occurrence of a steady deformation among other simultaneous deformations is sufficient evidence that true viscous deformation occurs.

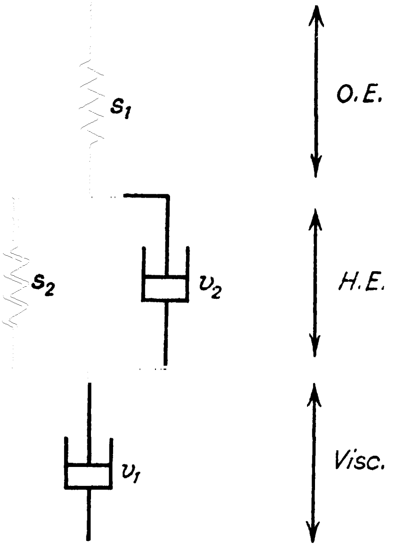


FIG. 36.—A simple arrangement of springs and dashpots illustrative of the types of deformation in high polymers.[37]

In order to overcome the difficulty of the lack of stress proportionality in the highly elastic deformation this term has been written in the form:[3]

$$D_{HE} = D_{HE\infty}(1 - e^{-t/\tau})$$

where $D_{HE\infty}$ is simply the limit of the highly elastic deformation occurring after a long time under the conditions of the experiment. However, this relation has required further modification and the suggestion has been put forward that D_{HE} be represented by a series of such terms, namely:

$$D_{HE} = \Sigma\, D_{HE_1}(1 - e^{-t/\tau_1})$$

In this connection Tobolsky and Eyring[65] agreed that a series of such terms can give a curve obeying the relation $D \propto \log t$ as found in some empirical treatments, but consider that the place exchange theory of Eyring (p. 112) affords a more useful approach. Naturally there are considerable difficulties in the way of applying such an unwieldy theory as that involving the summation of a large number of elasticity terms, but the treatment retains the advantage over the purely empirical approach, that the relaxation times are capable of logical relation to the temperature through the energy of activation u where u is given by

$$\tau = ke^{-u/RT}$$

It also follows as a further consequence of this theory of a range of relaxation times that a steady time-dependent deformation cannot be taken as evidence of true viscous flow since a large highly elastic deformation with a long relaxation time can give a similar deformation time effect.

Effect of Molecular Weight on the Time Factors in Highly Elastic Deformation

A relaxation time form of treatment has been used by Flory[56] as a method of investigating the effect of initial molecular weight on the rate of deformation of unvulcanized butyl rubber. When this rubber is stretched a large deformation takes place quickly, but further small deformations occur if the material is maintained under constant stress over a period of time. Plots of this slow deformation in the form of log α against time (where α is l/l_0 as before) are nearly linear and Flory took the slope after 10 min. when $\alpha = 1 \cdot 5$, as the standard measure of the rate of deformation.

From this he showed it was possible to derive the constant of stress relaxation which would have been observed if the material has been kept at constant elongation. This was expressed in the form:

$$\left(\frac{\delta \, lnG}{\delta \, lnt}\right)_{\alpha} = 1 \cdot 5$$

Where G is the parameter in the relation: Stress $= G.fn(\alpha)$. Plots of this quantity against $1/M$ are again linear (Fig. 37).

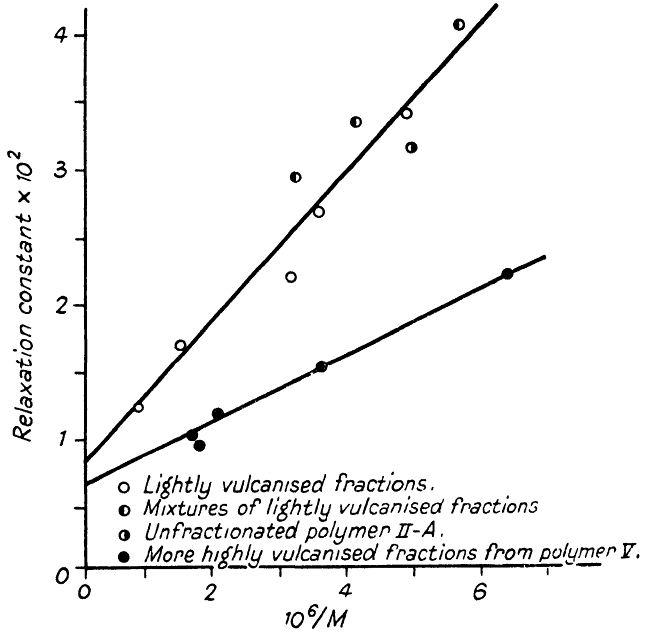


FIG. 37.—The relaxation constant of a butyl rubber plotted against the reciprocal of the molecular weight of the original unvulcanized polymer (M).[56]

A similar but more simple treatment of the same problem has been given by Rehner.[66] He plotted the quantity $(D_{(60\ \mathrm{sec})} - D_{(10\ \mathrm{sec})})$ against $1/M$ and again obtained a linear relation. His experiments, which were also carried out with polyisobutylene, were made with a plastometer arrangement in compression and were considered to be sufficiently accurate to be used as a routine method of checking molecular weights.

In another series of experiments also carried out with butyl rubbers Zapp and Baldwin[67] investigated the effect of altering the molecular weight distribution on the force required to compress a moulded cylindrical pellet to 50 per cent of its height in 10 sec.; they found this force was greatest with a pure fractionated polymer and decreased as the range of the molecular weight distribution increased. The rate of elastic recovery when the stress was removed was also found to be generally higher with the narrow distribution of molecular weights. Thus, it is to be expected that in a normal plastic the rates of deformation will be affected not only by the number, or weight, average molecular weights but also by their distribution.

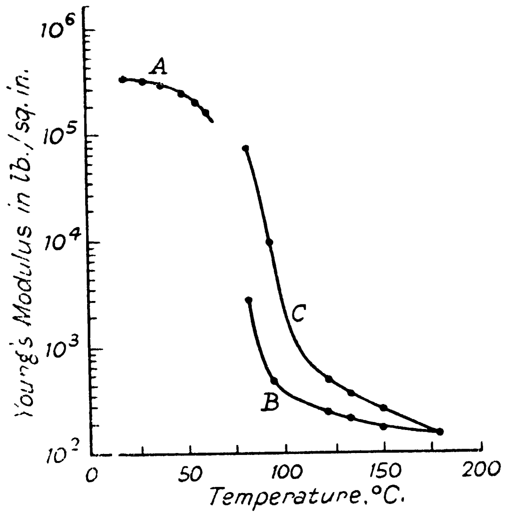


FIG. 38.—The Young's Modulus of polymethyl methacrylate fibres plotted against temperature. (*A*) From quick acting testing machine. (*B*) From total elongation of fibre. (*C*) From instantaneous elongation of fibre.[68]

Experimental Application of the Relaxation Time Treatment

An example of the application of relaxation theories to polymeric materials is given by the work of Robinson *et al.*[68] on methacrylate fibres. They assess an elastic modulus by different methods and find a marked fall over the range of elastic transition from 70 to 100° C. (Fig. 38), and the investigation of volume changes by the method of Ueberreitter gives a transition temperature of 71·1° C. (Fig. 39). The difference between this figure and that quoted by Tuckett from Alexandrov and Lazurkin being presumably due to the use of fibres and differing time-stress conditions. In long time deformation experiments curves like those of Fig. 40 are obtained, using loads of such a character that the total deformations obtained go up to about 10 per cent. The experiments were made in or above the region of elastic transition where the deformations were shown to be roughly proportional to the stress.

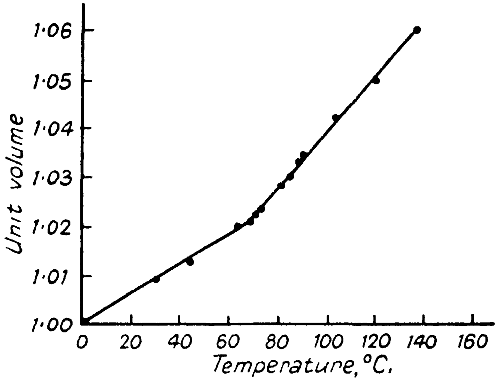


FIG. 39.—The dilatometric transition point of polymethyl methacrylate.[68]

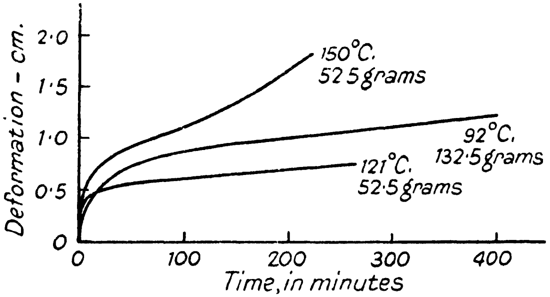


FIG. 40.—The deformation of polymethyl methacrylate fibres under constant load.[68]

The authors then analysed the deformations in terms of a Hookean modulus, three delayed elastic extensions, and a deformation proportional to the time which is treated as a viscous deformation. They show that two of the delayed elastic deformations give linear plots of log (relaxation time) against the reciprocal of the absolute temperature, and so may be related to activation energies. It should be noted that these experiments were made at relatively high temperatures and small deformations when the highly elastic forces are most likely to be controlling and to be approximately proportional to the stress. However, the application of methacrylate as a plastic generally involves the subjection of the material to all sorts of stresses mostly in the temperature range 0 to 30° C., and a theory of strength must also consider behaviour under these conditions however difficult it may be.

A very interesting application of the relaxation time treatment to a number of rubbers has been presented by Tobolsky and Andrews.[69] They distinguished between three temperature ranges in the behaviour of rubber-like materials. At intermediate temperatures the deformation at a particular stress (or vice versa) quickly reached a steady value which could be explained by the theory of high elasticity. At high temperatures the deformation at a given stress, which at first approximates to that given by equilibrium theory, gradually increases with time; and at low temperatures the deformation is initially less than the equilibrium deformation but gradually approaches it. Similar relations are observed if the relaxation of stress at constant deformation is studied, and the higher temperature behaviour is simpler than with deformation owing to the formation of secondary linkages during the process of creep.

Curves for the relaxation of stress at different temperatures corrected for temperature proportionality according to the theory of high elasticity are given in Fig. 41. In the quantitative investigation of these relations it was found that the high temperature stress relaxation was capable of a particularly simple treatment, only one relaxation time being necessary at any particular temperature. These relaxation times could be correlated through an activation energy of 30·4 k. cal. Tobolsky and Andrews further demonstrated that the characteristic high temperature relaxation only occurred in the presence of oxygen, the relaxation times being a thousandfold greater in nitrogen, and concluded that the process was one involving the scission of primary bonds identical to that occurring in the ageing of rubber. In the case of low temperature stress relaxation the curve was not of a simple Maxwellian form though the different curves obtained all appeared to be of a similar shape.

In another paper Tobolsky and Stern[70] extend the application of the relaxation theory to the case of polysulphide rubbers; the relaxation of stress in the range 35 to 120° C. could again be represented by a single relaxation time at a given temperature, and the results at different temperatures could be correlated through an activation energy of 25 k. cal. In this case also, stress relaxation behaviour was simpler than creep. However, a point of contrast emerged in that with the polysulphide rubbers the process of stress relaxation was independent of the presence of oxygen. Thus it can be said that the results of Tobolsky and his co-workers confirm the value of the relaxation time theory in explaining the behaviour of rubbers in the higher temperature ranges.

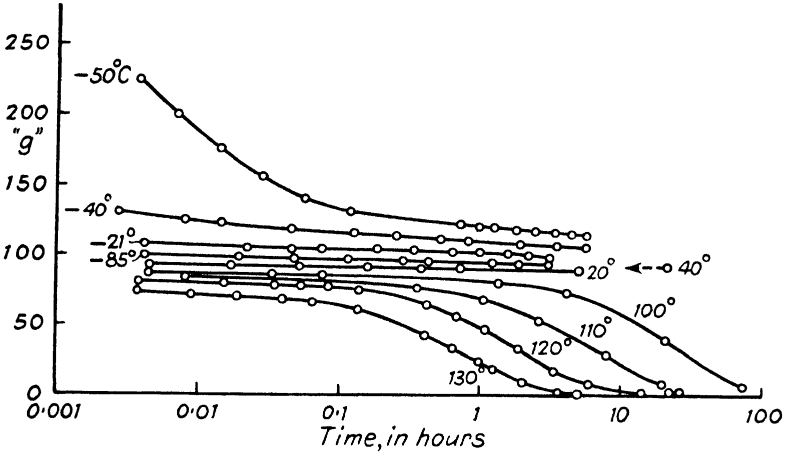


FIG. 41.—Elastic modulus curves based on the stress relaxation of natural rubber at different temperatures.[69]

Empirical Treatment of Deformation

From the strictly practical angle the theory of relaxation times frequently suffers from a lack of directness and simplicity in approach, for instance, where more than one relaxation time is required to account for the results obtained, and for this reason methods of treatment have been developed by rheologists which allow for a quantitative description of deformation processes without the necessity of disengaging all the complicated mechanisms involved, and without necessarily distinguishing between D_{HE} and D_{visc}. This work was begun by Scott Blair, whose work on firmness will be further discussed in the next chapter, and by

Nutting,[71] who first used the following equation to describe the deformation of certain materials in shear:

$$D = \psi S^{\beta} t^{k}$$

where ψ, β and k are constants characteristic of the material.

The same equation has subsequently been used successfully to describe the results of other types of deformation experiment. Application of this equation to discover the effect of stress on the deformation of plastic materials usually gives values of β greater than unity, i.e. the rate of deformation increases more rapidly than the stress, though values of 0·6 have been reported by Scott Blair[72] for certain filled phenolic resins. Characteristic high values have been obtained by Nutting[73] for a paint, and by Haward,[74] using a modified form of the equation, and the results of Press,[75] and Couzens and Wearmouth[76] further illustrate rates of deformation increasing more quickly than the stress. With some materials this rate of increase is so great after a particular stress is reached that a definite "yield point" may be satisfactorily employed to describe the deformation, i.e. a stress is postulated above which non-ideal deformation occurs and below which it does not take place. This increase in rate of extension with comparatively small increases in stress is illustrated in Fig. 42 for the extension of cellulose acetate under constant load.

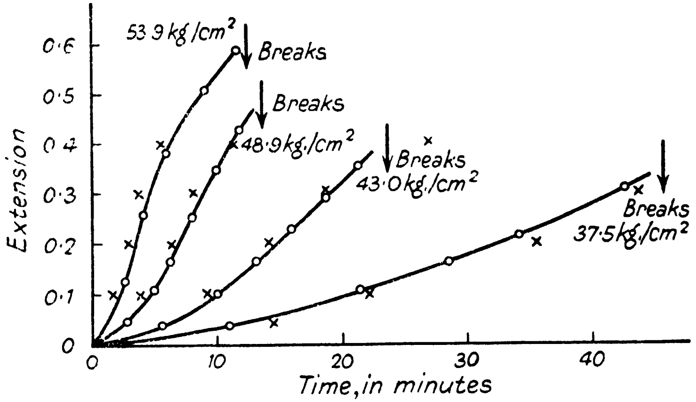


FIG. 42.—The non-ideal deformation of plasticized cellulose acetate film under constant load.[74]

With regard to the effect of time on the deformation of plastic materials the changes taking place in k, the time index, under

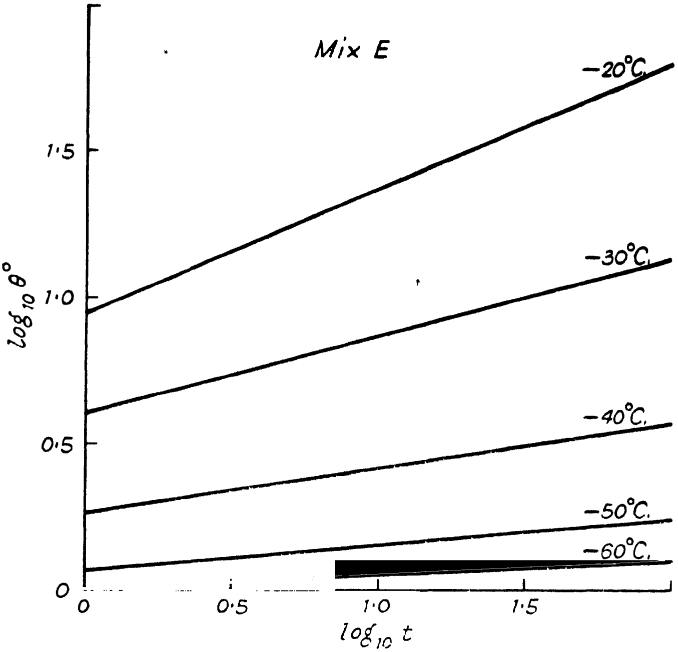


FIG. 43.—Logarithmic plots of torsional deformation against time for plasticized polyvinyl chloride.[77]

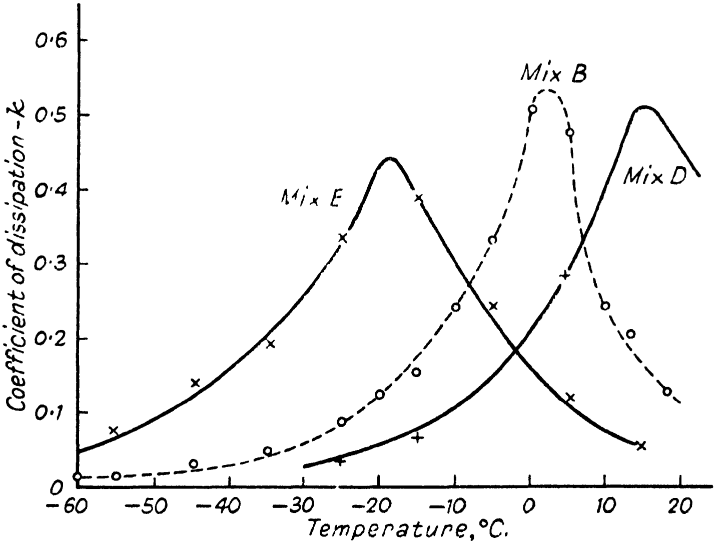


FIG. 44.—The variation of "*k*" the index of time dependency or "coefficient of dissipation" with temperature for plasticized polyvinyl chloride.[77]

differing conditions have been illustrated by the work of Bilmes,[77] who investigated the properties of plasticized polyvinyl chlorides in a torsion apparatus over a range of − 70 to 100° C. He used torques such that the angle of deformation was less than 120° in 100 sec. and obtained straight lines for plots of log (torsional deformation) against log (time) (Fig. 43) and approximate proportionality with stress ($\beta \simeq 1$). In this way he made measurements of k and also of ψ, the former illustrating the extent to which the

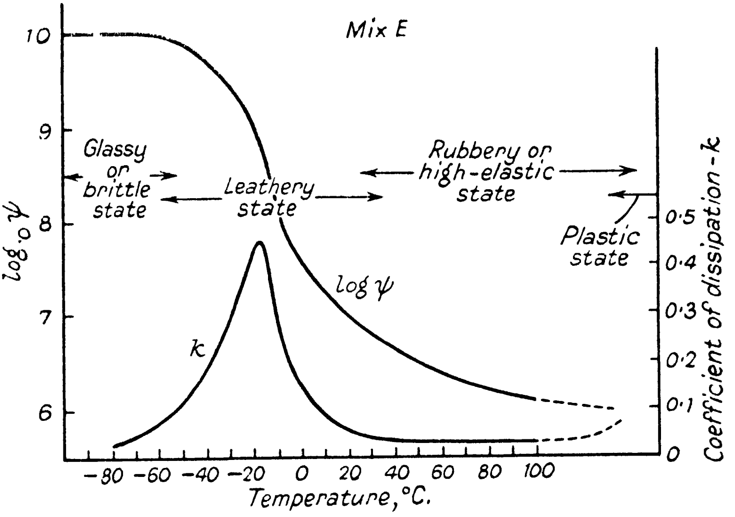


FIG. 45.—The changes of state of plasticized polyvinyl chloride in terms of the constants ψ and k in the Nutting equation.[77]

deformation depended on time and the latter the "elastic modulus" of the material. Where the time effects are zero a small ψ corresponds to an elastic modulus which can be given real meaning. The behaviour of k at different temperatures (Fig. 44) led Bilmes to describe his material as passing through four distinct states as the temperature is raised, namely: the glassy state ($\psi > 10^{10}$), leathery ($\psi\ 10^{10} - 10^{7}$), highly elastic ($\psi\ 10^{7} - 10^{6}$) dynes/in.^{2} and plastic states (Fig. 45).

It will be seen that the "leathery" state corresponds with the peak in the value of k, i.e. in the time-sensitivity, and also approximately with the period of rapid change in elastic modulus illustrated for another material in Fig. 35. Most plastics and rubbers will therefore show the properties of this state at some temperatures and its importance in use will depend on whether these are the temperatures at which the material is to be applied and also whether the transition to the true rubbery condition is sharp or spread out over a considerable temperature range. The curves for cellulose acetate (Fig. 42) with the marked time element involved may also be regarded as descriptive of the "leathery" state, although the values obtained for ψ do not agree with those obtained by Bilmes owing to the high values of β and the consequent dimensional heterogeneity of the equation.

In what Bilmes described as glassy state the material is hard and likely to be brittle; all the types of deformation depending on molecular rearrangement are suppressed, and as with massive glass, deformation tends to that of an ideal Hookean solid. It is probable that at sufficiently low temperatures most plastics will show pure Hookean behaviour but care must be used in applying the criteria of Bilmes to other plastic materials. For instance, the celluloid investigated by Haward[74] had a Young's modulus of 17,000 kg./cm.^{2} ($1 \cdot 7 \times 10^{10}$ dynes/cm.^{2}) and therefore just fell into the region of the glassy state but nevertheless was capable of yielding a non-ideal deformation of > 30 per cent when subjected to stresses of > 300 kg./cm.^{2} which did not break the material; in other words the value to which the overall "elastic modulus" must fall in order to indicate truly "glassy" behaviour varies from one material to another.

Limit of Extensibility

Recent work on the properties of cellulose derivatives in solution have yielded evidence that the disposition of cellulose chains may well be very different from the state of random disorganization assumed in the case of rubber molecules. Experiments by Mosimann,[78] and Campbell and Johnson[79] both lead to the result that the distance between the ends of the chain of dissolved cellulose nitrate approximates, except in the case of the longest molecules, to that of the fully stretched chain alone, and even with the highest degrees of polymerization only a very moderate amount of kinking can be assumed. The results given in Table XIX taken from the work of Mosimann illustrate the axial ratios of cellulose nitrate molecules calculated for the completely stretched chain and also from experimental work on solutions.

These results receive further support from the work of Doty, Zimm and Mark,[80] who showed that the light scattering phenomena given by cellulose acetate in acetone solution corresponded with a relatively extended molecular configuration as contrasted with that of polystyrene dissolved in methyl ethyl ketone where evidence of a kinked configuration was found.

Other experiments leading to generally similar results have been described by Gralén,[81] together with a full account of the theoretical treatment involved. However, the precise significance of this evidence has recently been questioned by Hermans,[82] who shows that some of Gralén's results do not require a completely rigid molecule but may also be explained by other assumptions, namely: in the cellulose chain there is still random kinking as between Kuhn's "statistical chain elements" (1*c* in formula 2, p. 81) but that in this case each chain element must be held to comprise of about 20 monomer units. Reference to Kuhn's formula shows that any such assumption will have the effect of greatly increasing the average distance between the ends of the chain, and so, for the purposes of a qualitative theory of deformation the assumption of an increased initial extension (the "span") for a cellulose chain remains justified in either case.

TABLE XIX AVERAGE EFFECTIVE AXIS RATIOS OF FIVE CELLULOSE NITRATE FRACTIONS COMPUTED FROM MOSIMANN'S DATA[78]

		Axial ratio calculated		
Molecular weight	D P	Completely stretched out molecule	Computed from sedimentation	Computed from frictional ratio
613,000	2,320	1,083	320	290
199,000	750	352	210	188
80,200	300	140	140	144
30,000	113	53	60	57
6,200	26	12	15	16

Thus, unless it is assumed that the cellulose nitrate molecule in a plastic composition is much more closely kinked up than in solution, it is impossible to assume the existence of anything precisely similar to the high elasticity of rubber with a cellulosic material, and its behaviour must be expected more to correspond to that of rubber in the region where large departures are found between experiments and theory owing to the straightening of the molecular chains. Clearly, even a slightly kinked chain can be straightened out and rearranged, but the processes involved when it is already nearly straight will be different from those taking place with a molecule in a randomly kinked condition. It follows that very definite limits are to be expected to the true highly elastic deformation of the cellulose plastics. In fact a limitation of 60 per cent in the deformation of a cellulose acetate gel was reported by Poole[83] and in his modified form of the Nutting equation

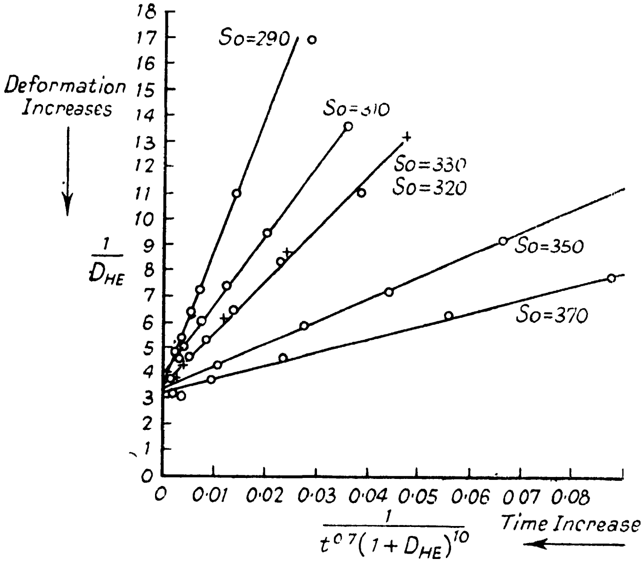


FIG. 46.—The non-ideal deformation of celluloid under constant load plotted so as to demonstrate the constant limit of extensibility at infinite time. So is the initial stress in kg/cm^2.[74] In spite of large differences in the rate of deformation all the lines converge on a similar final value.

Haward[74, 84] found it necessary to introduce a constant corresponding to a limit of highly elastic extensibility of 50 per cent for cellulose acetate and 30 per cent for cellulose nitrate.

This treatment showed that the apparent increase in the rate of deformation which sometimes occurs when a cellulose ester film is stretched under constant load may be quantitatively ascribed to the increase in stress as the cross-section diminishes. The results could be reduced to a linear form so that approximate estimates of the limit of deformation could be made even when the material fractured at about half the maximum extension. Results for celluloid are given in Fig. 46. It will be seen that as the time increases ($1/t^{0·7}$ decreases) the lines at different stresses all converge on much the same value of $1/D_{HE}$ and that these approximately correspond to a value of $D_{HE} = 0{\cdot}3$ (30 per cent).

This limit of a highly elastic deformation (which was shown to be reversible on warming) was ascribed by Haward and also by Tuckett[37] to the relatively stretched out character of the cellulose chain as deduced from steric considerations. With a plasticized cellulose acetate this limit of extension, as would be expected in the case of structural feature, does not appear to vary markedly either with the temperature or the stress, and as a result of his extension experiments on cellulosic and other materials Haward concluded that this limit of the potentially reversible highly elastic deformation was one of the fundamental properties of a plastic and largely influenced by the structure of the chain. Some approximate figures for this property at normal temperatures are given in Table XX for a few high polymers.

TABLE XX. LIMIT OF HIGH ELASTICITY OF SOME PLASTIC MATERIALS

Material	Approximate limit of highly elastic deformation
	%
Natural rubber	700–1,000
Plasticized polymethyl methacrylate	500
Plasticized polyvinyl butyral	300[85]
Cellulose acetate 40% dimethyl phthalate .	50
Cellulose nitrate—camphor sheet (celluloid) ..	30
Swollen cellulose fibres	400[86]

The word approximate is emphasized. If the differences were not so large the figures could not be regarded as significant.

A good deal of attention has been given to the problem of the maximum deformation of cellulose fibres by Hermans.[86, 87, 88] Firstly he demonstrated the differences in maximum extensibility between cellulose and various rubbers in general terms (Fig. 47) and he then went on to investigate the particular characteristics of the cellulose fibre. He found that the deformation was only partially reversible, whereas with plastics the slow limited deformation is at least potentially reversible in that full contraction will occur on warming. This was found by Haward for plasticized cellulose acetate and nitrate and methyl methacrylates. Similarly Aiken, Alfrey Janssen and Mark[89] found that all the creep deformations of a plasticized vinyl chloroacetate polymer were fully recoverable. To explain his results Hermans suggests that crystallization is playing a major part in the deformation process and that new linkages which are not readily broken up are formed between the chains during the extension. From the strictly rheological point of view, therefore, these deformations can hardly be classed as of the highly elastic type, though they are treated as such here on the assumption that they are also concerned with the

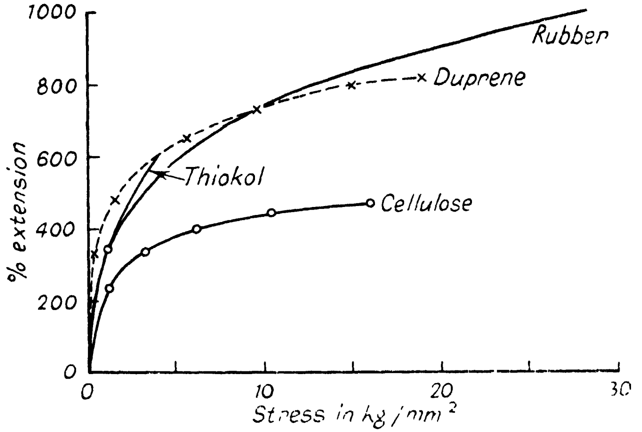


FIG. 47.—Deformation-load curves for rubber and cellulose fibres.[86]

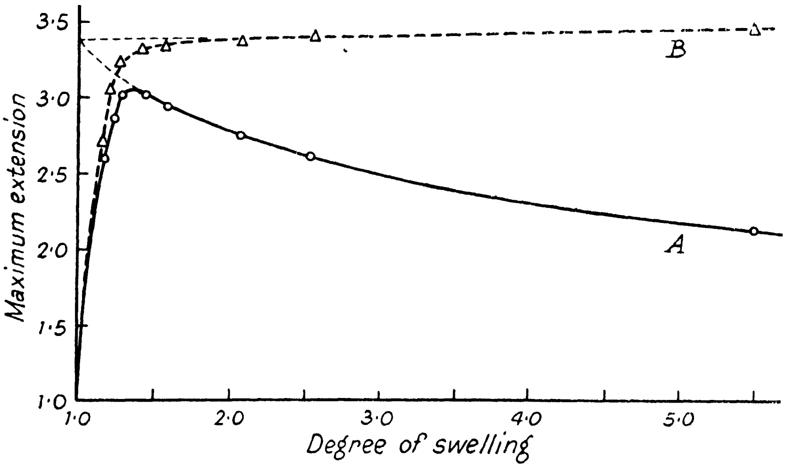


FIG. 48.—The maximum extensibility of swollen cellulose fibres in relation to the degree of swelling. Curve (*A*) is based on the wet length and (*B*) on the dry length of the fibres.[88]

straightening out of polymer chains. This assumption is also made by Hermans, who notes that deformations above 100 per cent could not occur in a system of linked rod-like particles[90] and therefore concludes that the cellulose molecules are at least partially kinked.

A particularly interesting point arose when Hermans investigated the relation between the maximum extensibility and the degree of swelling of a wet cellulose fibre[88] (Fig. 48). If the maximum extension is related to the initial length of the swollen fibre it first rises and then falls with the degree of swelling (curve A), but if this extension is referred to the dry length of the same fibre it is found that the final deformation becomes constant when the degree of swelling is above 1·3 (curve B). Presumably a small amount of water is necessary to facilitate the chain extension process at stresses below the breaking strength of the fibre; it follows that the maximum extensibility is inversely proportional to the cube root of the swelling ratio. Obviously, if this system is analagous to that of a plasticized polymer the somewhat unexpected conclusion is reached that an increase in plasticizer content over a certain amount will reduce the maximum extensibility of the material.

Another factor which affects the limit of extensibility of a polymer is the occurrence of crystallization. This plays a considerable part in determining the mechanical properties of rubbers and especially of natural rubber, but is absent in many of the common plastics which do not crystallize (e.g. polymethyl-methacrylate, polystyrene, vinylacetate[90a]). In the case of a natural rubber vulcanizate, Gee[90b] has shown that when the temperature at which the experiment is carried out is raised from 20° C. to 70° C., the deformation at 1,000 kg/cm^2 (actual cross-section) increases from 550 per cent to 650 per cent. The difference is explained by the greater amount of crystallization occurring at the lower temperature. In the case of rubber, it also seems unlikely that the long chain molecules will be effectively straightened out even by an extension of 800 per cent. For this reason, Meyer and Van Der Wyk[91] have suggested that the chain straightening only takes place in portions shorter than the whole molecule, so that a felt is formed (Fig. 49). According to Gee,[90b] the felted portions of different molecules would be largely incorporated into the crystalline phase. From either point of view, the molecules are not easily extended further.

Another example of limiting extensibility has recently been given by Speakman,[92] who has shown that a keratin fibre deforms in such a way that it tends to a limit of 70 per cent extension. From this observation, he draws conclusions about the folding of the molecules concerned.

If we are correct in assuming that a limit of highly elastic deformation plays a considerable part in the large deformations of plastic materials it follows that these properties cannot be adequately represented by the conventional spring and dashpot models. In the characteristic case such a material will show a constant deformation limit at long times, approximately independent of stress, provided that viscous flow does not occur and that rupture does not take place before the final deformation is approached. The general conditions favouring such properties in plastics are those in some degree characteristic of the low temperature conditions observed by Tobolsky and Andrews[69] (Fig. 41); here the internal resistance or viscosity of the material is so large that the stresses required to cause deformation at a measurable rate are large compared with the forces of elastic retraction at moderate extension and the deformation proceeds directly to the maximum value where the chains are straight (or felted). The final deformation is controlled by that part of the stress-strain curve which is nearly parallel with the stress axis and is therefore approximately independent of the stress. However, the possibility of actually measuring the maximum deformation in a particular experiment will depend on the time allowed and on whether the fracture process overtakes the deformation before the limit is reached. Experience suggests that this tends to happen increasingly as the temperature is reduced, until, in the glassy state, the plastic is broken before any appreciable amount of non-ideal deformation can occur.

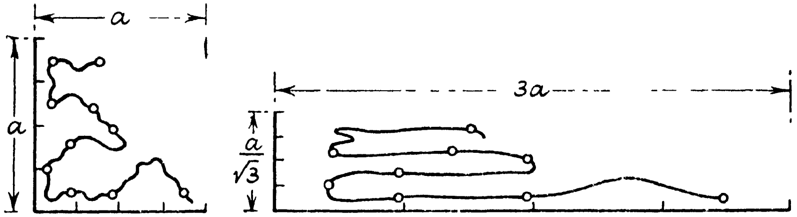


FIG. 49.—A model suggested to explain the limited extensibility of rubber.[91]

It has been stated that deformation under the conditions discussed above cannot readily be treated by means of the relaxation time approach, but the work of Robinson *et al.*[68] suggests that this method can conveniently be used when small slightly delayed deformations occur at low stresses. In these circumstances the ordinary forces of high elasticity control the deformation before the limit of extensibility is approached and the spring and dashpot models are therefore relevant.

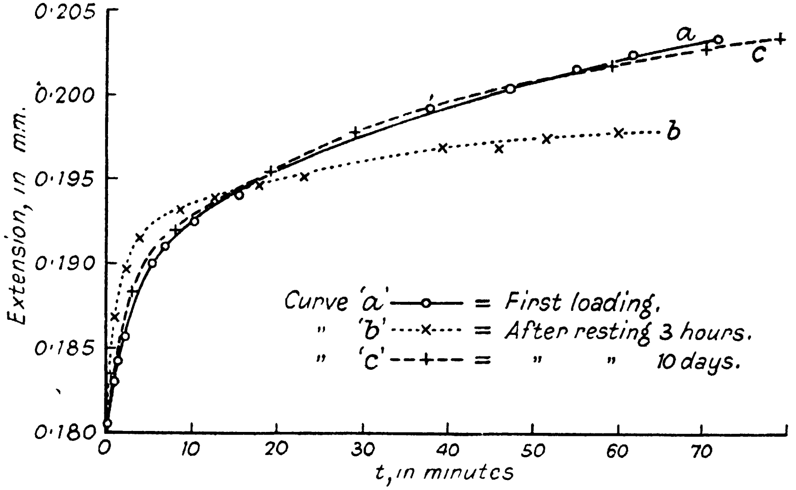


FIG. 50.—The small time dependent deformations of celluloid, occurring at the end of a larger, ideal, Hookean deformation.[93]

Finally, reference may be made here to the existence of some small slow deformations in the range between the true Hookean deformation and the highly elastic process. These were ignored by Haward, who allowed for the Hookean deformation (< 2 per cent) and then measured the much larger highly elastic deformations, but Coker and Filon[93] have described some small time-dependent deformations obtained with celluloid (Fig. 50) which amounted to about one-sixth or less of the initial (ideal Hookean) strain. These results are of considerable interest in that they favour the view that variations of Hookean elasticity with temperature may be due to small delayed elastic effects. If changes in temperature are assumed to be equivalent to altering the time in which elastic deformation is measured it is clear that variations in this modulus are possible, due to incorporating more or less of these delayed elastic effects. Coker and Filon showed that the results could be represented by a relation of the type $D = a + bt^{1/3} + ct$ and thus they implicitly recognized that the deformation of plastic materials was not all of one kind.

Viscous Flow

It is probable that true viscous flow is a rarer phenomenon with high molecular weight materials at normal temperatures than a first perusal of the literature would lead one to believe. Certainly the existence of apparently irreversible deformations under stress cannot be accepted as final proof that viscous flow has taken place. This subject has been considered by Gurevich and Kobeko,[94] who quote an interesting case of a moulded bar of polystyrene which, when heated to 150° C., returned approximately to the original shapes in which it had been polymerized; only a very limited amount of flow had occurred during the moulding process and the bar had been shaped through deformation of the highly elastic type. The same workers also reviewed some experiments by Church and Daynes[95] on ebonite which showed that if this material is twisted through an angle of 20° the amount of apparently permanent deformation remaining after removal of the torque, is a maximum over a short temperature range and less at temperatures above and below. According to Gurevich and Kobeko these results are due to the occurrence of a predominantly ideal (immediately reversible) Hookean deformation at low temperatures and to the reversibility of the highly elastic deformation at higher temperatures. In the intermediate range the delayed high elasticity is not readily reversible as the elastic forces may not be greater than the frictional forces opposing the molecular rearrangements, and the apparently irreversible deformation therefore reaches a maximum. Thus, in this case, what appears to be viscous flow is actually a highly elastic deformation.

Unless appreciable amounts of flow take place comparable with other types of deformation, viscous flow has only a specialized importance in strength tests where the irreversible nature and the consequent permanence of the changes brought about by it are significant. However, the whole question has a considerable importance in connection with the suitable temperatures and conditions for moulding, and has been discussed by Tuckett.[96] In this treatment the ideal Hookean deformation is neglected in comparison with other types of deformation and we write for D the deformation in time t, namely:

$$D = D_{visc} + D_{HE}(t)$$
$$= Ate^{\frac{-E_{visc}}{RT}} + D_{HE\infty}(1 - e^{-t/T})$$

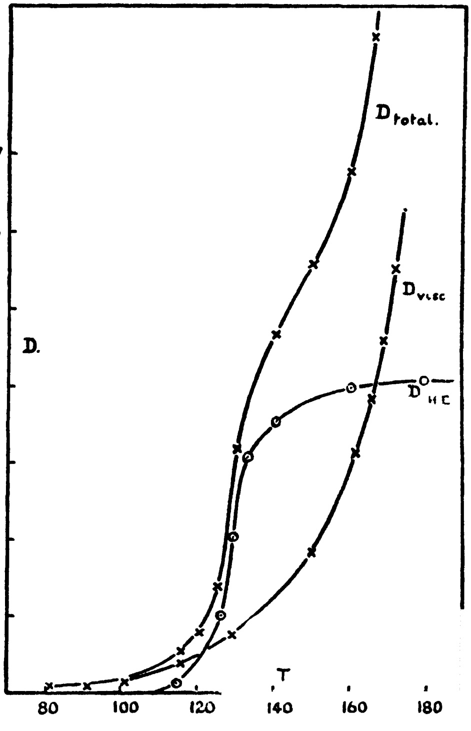


FIG. 51.—Theoretical curves for the temperature dependence of highly elastic and viscous deformations.[96]

where E_{visc} is the energy of activation for viscous flow and the viscosity term is formulated in the simplest way.

Although the high elasticity term in this equation may differ according to the stress employed, the relation does give an indication of the relative behaviour of the two types of deformation. The resultant and particular deformations are illustrated in Fig. 51 taken from Tuckett's paper, where the highly elastic deformation is taken from the work of Alexandrov and Lazurkin[3] and the viscous deformation is based on an assumed energy of activation of 20,000 cal./gm. mol. The relative positions of the two curves could easily be displaced, but the results indicate the characteristics of the two types of deformation and in particular the limit to which, according to the relaxation time theory, D_{HE} tends at a given stress as the temperature is raised or the time increased, and also the continuous character of the viscous process.

Taking the above relation, if $t/\tau < 10^{-1}$ then

$$D_{HE} = D_{HE}\, t/\tau \text{ approximately}$$

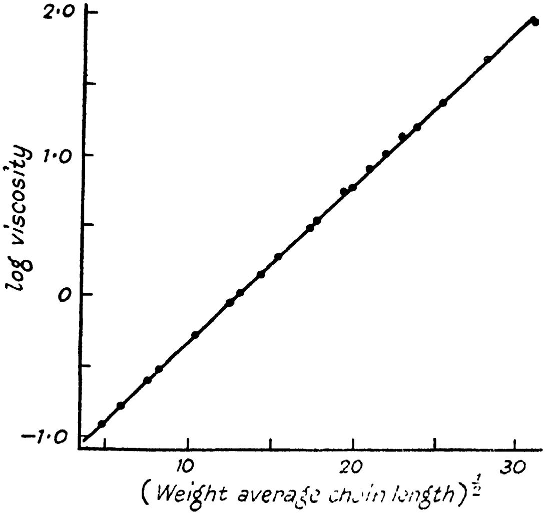


FIG. 52.—The melt viscosity of a linear polyester plotted against the square root of the molecular weight.[97]

thus for times short compared with the relaxation time a material whose highly elastic deformation followed this relation could not be distinguished from one showing plastic flow by a pure deformation experiment.

The amount of viscous flow is markedly dependent on the molecular weight of the polymer concerned and Flory[97] found that with linear polyesters the logarithm of the viscosity was proportional to the square root of the molecular weight as shown in Fig 52, thus the viscosity of a polymer may be represented by the relation

$$\log \eta = \lambda + \mu\,(M_w)^{\frac{1}{2}} + \frac{E_{visc}}{RT}$$

and on this basis Flory found that E_{visc} was independent of molecular weight and varied from 8,050 cal./gm. mol. for decamethylene sebacate to 8,550 cal./gm. mol. for decamethylene succinnate.

Basing his procedure on these conclusions and taking the softening point as an iso-viscous measurement Tuckett concludes that where a true softening point (T_s) is being measured unaffected by elastic effects

$$\mu \sqrt{M_w} + E/RT_s = \text{constant}.$$

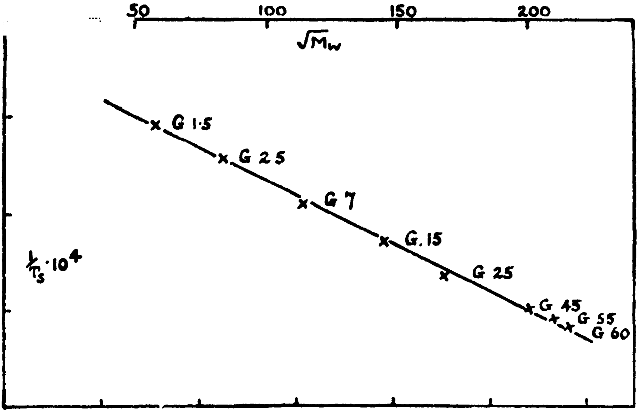


FIG. 53.—The reciprocal of the absolute softening temperature plotted against the square root of the molecular weight for polyvinyl acetate.[96]

This relation is obeyed for measurements on vinyl acetate polymers by Morrison[98] (Fig. 53). On the other hand where the softening point measurement is not based on viscous flow alone these relations should be curved, and such relations are obtained in the vinyl acetal series.

Flow occurring under deformation at normal temperatures was investigated by Treloar with rubber,[99] taking extreme precautions to obtain full recovery of the elastic part of the deformation. The strips of strain free rubber were extended for 1 hour at 25 and 50° C. and then allowed to recover as much as possible at the same temperatures. Further recovery was then brought about by swelling in mixtures of benzene and alcohol. The results showed that irreversible plastic flow was much larger at 50° C. than at 25° C. and at the latter it was always small compared with the elastic deformation. The outstanding feature of the experiments was that plastic flow was found to rise to a maximum at a given deformation of the rubber (300 to 400 per cent depending on the temperature), and when the rubber was held at deformations above and below this maximum much lesser amounts of plastic flow were obtained. Treloar interprets the results as follows: flow increases with the deformation until crystallization takes place and operates to reduce the amount of flow. However, the extent to which this mechanism may operate in other cases is not clear since Astbury[100] has shown that the marked crystallization occurring with rubber and some other polymers is by no means general with many common plastics (e.g. methacrylate).

A Molecular Theory of Flow

So far no fundamental theory has been described which attempts to account for all the various effects associated with the action of a stress on plastic materials. The phenomena concerned are extremely complicated and it is unlikely that any simple law can be discovered which will cover all the observed cases, but the theory of *viscous flow* put forward by Eyring[101] does seem to satisfy a considerable range of observations, and would appear to justify a wider application to experimental results. Further, although the theory has been developed in connection with viscous flow, it may prove to be capable of application to the highly elastic deformation of plastics in the "leathery" state where viscous forces play a major part in opposing the deformation of the material. However, wherever the deformation is comparable to the limits of highly elastic extension some further correction would no doubt have to be introduced to allow for this condition.

According to the Eyring theory the viscous flow process is the consequence of the movement of a molecule, or a segment of a molecule, from one equilibrium position to the next. If E is the height of the potential barrier to be crossed between the two positions, the frequency with which such steps occur under the influence of the thermal agitation will be proportional to $e^{-E/RT}$.

If now a stress S is applied to the system this energy barrier becomes modified to $E - bS$ in the direction of the stress, where b is a constant, and to $E + bS$ in the opposite sense. In these circumstances the rate of movement of molecules in the direction of the stress will be

$$= k\, e^{-(E-bS)RT}$$

and in the opposite direction

$$= k\, e^{-(E + bS)RT}$$

Hence, the net rate of flow

$$= k\, e^{-E/RT}\left(e^{bS/RT} - e^{-bS/RT}\right)$$

$$= 2\, k\, e^{-E/RT} \sinh \frac{bS}{RT}$$

Now if $bS \ll RT$ this rate of flow becomes proportional to S as sinh bS/RT reduces to bS/RT and the system behaves as a Newtonian liquid. However, in the case of stiff plastic materials relatively large forces may be applied and bS may become $\gg RT$. Under such conditions the equation approximates to

$$\text{rate of flow} = k\, e^{-E/RT}\, e^{bS/RT}$$

$$\text{i.e. } \log (\text{rate of flow}) = \text{constant} + K.\,S.$$

Now it is clear that in many cases where the Nutting equation has been applied over a short range of stress the difference between a log (rate) — log S relation and a log (rate) — S curve will not be large, and results complying with one form will at least approximately agree with the other. In other cases, as in the work of Sheppard *et al.*,[102] a linearity between log (rate) and S has been reported for a deformation described as "plastic" flow but probably involving highly elastic components, and this treatment may be capable of a wider application in the deformation of plastic materials.

On the other hand, Eley and Pepper[103] have found that the various stress effects occurring with a soft plasticized cellulose derivative could not be brought within the framework of the Eyring method and that, above a certain stress S_o the material follows the equation originally used by Bingham to describe the flow of solid liquid dispersions, namely:

$$S \geqslant S_o \text{ rate of flow} = \text{const. } (S - S_o).$$

However, the plastic investigated by Eley and Pepper did not show a true yield value and it was possible to observe flow at stresses well below the apparent yield stress. These authors conclude that a critical attitude must be taken up towards the place-exchange theories put forward by Eyring, and that other complicating factors will have to be considered. At present there appears to be little published experimental evidence directly related to the Eyring equation but it would obviously be a great step forward if it could be shown that the effect of stress on viscous flow or elastic deformation was capable of being related to a comprehensible activation process.

Deformation of Thermosetting Materials

The amount and complexity of the experimental evidence available describing the deformation of the thermosetting resins is less than that on thermoplastics, probably because the characteristic time-dependent deformations occurring with thermoplastics are present on a much reduced scale in the thermosetting series at normal temperatures. So the behaviour of a phenolic resin is better represented by its moduli of ideal Hookean elasticity than with the other plastics. For instance, as the result of bending tests, Hazen[104] concluded: "the great majority of phenolic plastic moulding materials and many other related materials show either no appreciable deviation or only relatively slight deviation from Hooke's law for all values of the applied load up to the breaking point." Some of the typical deformation properties of thermosetting plastics are illustrated in a paper by Telfair *et al.*,[105] where various simple and complex materials are subjected to small deformations ($< 0{\cdot}5$ per cent), and the time effects noted. The scale of the deformations is probably characteristic of the materials

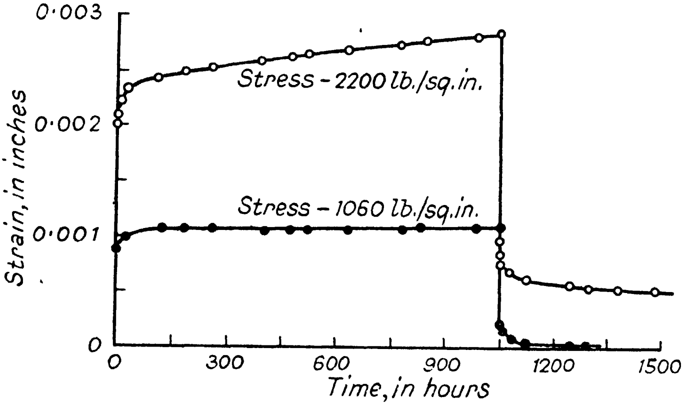


FIG. 54.—Deformation and recovery curves for a wood flour-filled phenolic resin.[105]

since rupture occurred in some cases, i.e. these materials could not easily be stretched further (Fig. 54). Clearly the reversible modulus is the dominating factor under these conditions, but noticeable time-dependent deformations also occur and may be important in certain applications. The authors go on to report that total deformations can be represented by a formula of the type

$$D = A \log t + b t + C$$

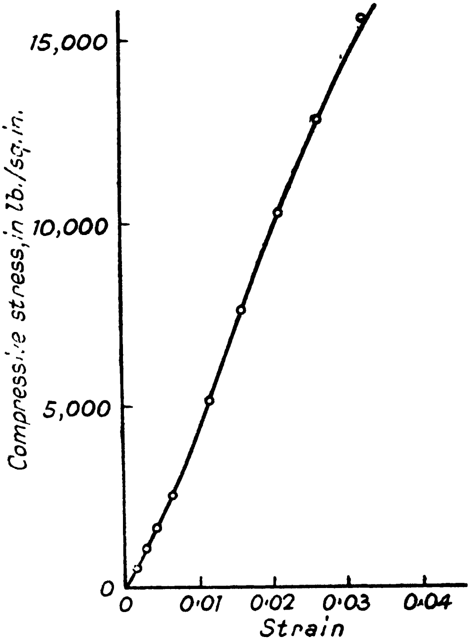


FIG. 55.—The deformation of a cresol resin in compression.[106]

A part of the time-dependent deformation is not recoverable under the conditions of the experiments, but this is not related to any particular terms in the above relation and the existence of a true viscous flow is uncertain. On the other hand, experiments are made at a series of temperatures and it is shown that both total deformation and the rate of deformation are increased two to fourfold if the temperature is raised from 77 to 190° F., but even under these conditions the extensibility does begin to approach that of a rubber. If phenolic and other thermosetting materials are capable of large deformations these can only occur at temperatures well above those at which the plastics are most often used.

The behaviour of cresol resins has been investigated by de Bruyne,[106] who found that they showed very definite departures from Hooke's law though phenolic resins showed more normal properties. If the behaviour of a cresol resin is investigated in compression the curve slope (Fig. 55) shows that the apparent modulus of elasticity at any given stress rises to a maximum and then falls as the stress is increased. It is probable that the fall in the modulus at high stresses indicates the occurrence of non-ideal deformations; indeed de Bruyne showed a delayed elastic component recoverable at 110° C. However, the increase in the modulus as the stress is raised at low stresses can hardly be ascribed to such an effect and the explanation remains obscure; it is not known if this somewhat anomalous result is to be observed with any other thermosetting resins.

Deformation measurements on phenolic and other materials have also been carried out by Sutton[107] on cylinders 12 mm. diameter and 12 mm. long in an investigation of the problem of compressive strength. The deformations were mostly small (< 3·0 per cent) and could be analysed according to an equation with three terms, namely:

TABLE XXI. THE COMPRESSIVE STRENGTHS OF CERTAIN PLASTICS ACCORDING TO VARIOUS DEFINITIONS

Material	Change in short time modulus	Change in k in term (t/k)	Onset of flow (Bt)	Nature of failure
Phenol A	600	750	500	Sudden collapse
Casein	500	600	380	Slow barrelling
Bakelite X 20	800	1,200	680	Collapse
Diakon (methacrylate)	500	540	340	Slow barrelling
Cellulose acetate ..	140	170	140	Slow barrelling

$$D = C + A(1 - e^{-t/k}) + Bt$$

where the time-independent part of the deformation gave a constant modulus of elasticity up to fairly high stresses, but eventually a stress was reached where this modulus appeared to change. Similarly, k was constant at low stresses but rose as the stress was increased beyond a certain point, but the constant B, which was regarded as measuring the rate of flow (without specific proof of irreversibility), depended on the stress above a certain yield point, i.e. there was a concave rate of flow-stress curve ($\beta > 1$ in the Nutting relation $D = S^{\beta} t^{k}$). In each case, above a particular stress, a change in behaviour was observed, and three different stresses could be measured to give separate criteria of compressive strength (Table XXI).

Information of this nature is a considerable advance upon any results obtained from a few arbitrary tests and holds out the hope of predicting safe behaviour in a variety of conditions. The work illustrates how, even in the present stage, deformation theory can be of practical value.

Tests Based on Deformation

A number of tests commonly applied to plastics and glass are, in fact, tests of deformation. Among these come a number of tests of hardness, and also certain brittle point determinations in which interest generally centres round the capacity of a material to sustain a given deformation applied quickly. Tests of deformation are not always meant to investigate the moduli of elasticity. For instance, in the prescribed method of testing toughened glass[108] the glass is subjected to a specific degree of bending under which it must not break. However, since most of the glass intended to be subjected to this treatment is a commercial mix with a reversible Hookean Young's modulus of 700,000 kg./cm.,^{2} the variable quantity that is really being investigated is the bending strength of the glass, and the result of the test actually depends on the static strength of the glass.

TABLE XXII. SUMMARY OF MAXIMUM PERMISSIBLE DEFORMATION IN CERTAIN COMPRESSIVE TESTS

Specification	Material	Stress	Permissible yield
		lb./in.^2	
B.S.S. 903: 1940 ..	Vulcanized rubber	Variable	0·4 mm. out of 12 mm.
B.S.S. 1137: 1943 ..	Synthetic resin bonded paper sheets	12,000	3%
B.S.S. 972: 1941 ..	Synthetic bonded fabric sheet	10,000	4%
A.S.T.M.:—D703—48T	Polystyrene	4,000	1·5% (50° C)

In brittle point tests, and also in folding tests and tests of elongation at break, the material should be able to give a deformation of a certain amount before fracture occurs. In these cases, *other factors being equal*, the materials with the lowest elastic moduli relaxation times, and limits of extensibility, etc., will do best. But in many conditions ability to withstand a stress without yielding (giving a deformation) is vital and therefore another series of criteria have been established by which the material must not be deformed beyond a certain extent under a given stress; these criteria are used for hard rubbers, polystyrene and thermosetting resins. Such limits have been incorporated into a number of specifications and naturally vary with the material being tested; their inclusion appears to be customary in compression tests when fracture is also measured. A summary of the contents of certain typical specifications is given in Table XXII.

Another test of a similar type is a "plastic yield" test; a cantilever of the material is loaded near one end and the deformation is measured after subjecting the beam to a particular temperature for a specified time. Generally a limit of 5 mm. deformation is allowed for a cantilever of effective length 145 mm. However, the precise conditions vary from one material to another and for full details the specifications should themselves be consulted (B.S.S. 771: 1938, B.S.S. 903: 1940). A further type of bending test is included in B.S.S. 1137: 1943.

Naturally these measurements only give a bare indication of the deformation properties of the material, but in practice their value is increased by designing each specification to suit a specific type of material. Further, in three of the four specifications in Table XXII the plastic material involved is of the thermosetting type and in the case of polystyrene the material is of a hard type, and this simplifies the information required, but in view of the considerations already mentioned in this chapter it is not surprising that the specification of deformation behaviour with the softer thermoplastic materials has not yet been very widely undertaken.

REFERENCES—IV

(1) PRESTON, F. W.: *J. App. Phys.*, **13** (1942), p. 623.

(2) GUREVICH, G.: *J. Tech. Phys. U.R.S.S.*, **4** (1937), p. 622.

(3) ALEXANDROV, A. P., LAZURKIN, T. S.: *Acta Physicochim. U.R.S.S.*, **12** (1940), p. 647.

(4) *Nature*, **149** (1942), p. 702: Report on British Rheologists' Club.

(5) MCNALLY, J. G., SHEPPARD, S. E.: *J. Phys. Chem.*, **35** (1931), p. 100.

(6) UEBERREITER, K.: *Zeit. Phys. Chem.*, **45 B** (1940), p. 361.

(7) BOYER, R. F., SPENCER, R. S.: *J. App. Phys.*, **15** (1944), p. 398.

(8) FUOSS, R. M.: *J.A.C.S.*, **63** (1941), pp. 369, 378, 385.

(9) MURGATROYD, J. B., SYKES, R. F.: *J. Soc. Glass Tech.*, **31** (1947), p. 17.

(10) MOREY, G. W.: *Properties of Glass* (Reinhold, New York, 1938).

(11) AUERBACH, F.: *Ann. d. Phys. u. Chem.*, **53** (1894), p. 1000.

(12) STRAUBEL, R.: *Ann. Physik. Chem.*, **68** (1899), p. 369.

(13) Jones, G. O., Turner, W. E. S.: *J. Soc. Glass Tech.*, **26** (1942), p. 35.
(14) Koenig, A.: *Ann. Phys. Chem.*, **28** (1886), p. 108.
(15) Winkelman, A.: *Ann. Phys. Chem.*, **61** (1897), p. 105.
(16) Strong, G. E.: *J. Am. Ceram. Soc.*, **20** (1937), pp. 16–22.
(17) Andrews, J. P., Lees, C. H., Shave, L. S.: *Proc. Phys. Soc.*, **36** (1924), p. 405.
(18) Haward, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 5.
(19) Ide, J. M.: *Rev. Sci. Instr.*, **6** (1935), p. 296.
(20) Sosman, R. B.: see G. W. Morey, Ref. 10 above, p. 297.
(21) Bhagavantam, S., and Rao, B. R.: *Nature*, **157** (1946), p. 625.
(22) Gehlhoff, G., Thomas, M.: *Z. Tech. Physik.*, **7** (1926), p. 105.
(23) Jones, G. O.: *J. Soc. Glass Tech.*, **28** (1944), p. 452.
(24) Badger, H. E., Silvermann, W. B.: *J. Am. Ceram. Soc.*, **18** (1934), p. 276.
(25) Birch, F., Dow, R. B.: *Bull. Geol. Soc. Am.*, **47** (1936), p. 1235.
(26) Taylor, N. W.: *J. Phys. Chem.*, **47** (1943), p. 235.
(27) Leaderman, H.: *Elastic and Creep Properties of Filamentous Materials and other High Polymers* (Textile Foundation, Washington, D.C., 1943).
(28) Jurkov, S.: *J. Tech. Phys. U.S.S.R.*, **1** (1935), p. 386.
(29) Murgatroyd, J. B.: *J. Soc. Glass Tech.*, **28** (1944), p. 368.
(30) Slayter, G.: *Mod. Plast.* (May 1944).
(31) Kuhn, W.: *Zeit. Phys. Chem.*, **47 B** (1940), p. 1.
(32) De Boer, J. H.: *Trans. Farad. Soc.*, **32** (1936), p. 10.
(33) Meyer, K. H., Lotmar, W.: *Helv. Chim. Acta.*, **19** (1936), p. 68.
(34) Houwink, R.: *Trans. Farad. Soc.*, **32** (1936), p. 122.
(35) Gloor, W. E.: *J. App. Phys.*, **12** (1941), p. 420.
(36) Gloor, W. E., Gilbert, C. B.: *Ind. Eng. Chem.*, **33** (1941), p. 597.
(37) Tuckett, R. F.: *Chem. and Ind.*, **62** (1943), p. 430.
(38) Bartoe, W. F.: *Aviation* (Jan. 1943), p. 126.
(39) *I.C.I. Plastics Technical Bulletin No.* 10 (1944), p. 10.
(40) Hauck, K. H., Rohs, W.: *India Rubber J.*, **108** (1945), p. 131.
(41) Rinehart, J. S.: *J. App. Phys.*, **12** (1941), p. 811.
(42) Mark, H., Press, J. J.: *Rayon and Textile Monthly* (June, July, Aug. 1943).
(43) Sack, H. S., Motz, J., Work, R. N.: *J. App. Phys.*, **15** (1944), p. 396.
(44) Sack, H. S., Motz, J., Raub, H. L., Work, R. N.: *J. App. Phys.*, **18** (1947), p. 450.
(45) Eley, D. D.: Private communication.
(46) Treloar, L. R. G.: *Trans. Farad. Soc.*, **40** (1944), p. 65.
(47) Meyer, K. H., Von Susich, G., Valko, E.: *Koll. Z.*, **59** (1932), p. 208.
(48) Kuhn, W.: *Koll. Z.*, **67** (1934), p. 2; **76** (1936), p. 258.

(49) GUTH, E., MARK, H.: *Mh. Chemie*, **65** (1934), p. 93.

(50) TRELOAR, L. R. G.: *Reports on the Progress of Physics*, **9** (1943), p. 113.

(51) MEYER, K. H., FERRI, C.: *Helv. Chim. Acta*, **18** (1935), p. 570.

(52) CASTON, A., GUTH, E.: *J. Phys. Chem.*, **46** (1942), p. 826.

(53) BUSSE, W. F.: *J. Phys. Chem.*, **36** (1932), p. 2862.

(54) WALL, F. T.: *J. Chem. Phys.*, **10** (1942), pp. 132, 485.

(55) GUTH, E. AND JAMES, H. M.: *J. Chem. Phys.*, **11** (1943), p. 455.

(56) FLORY, P. J.: *Ind. Eng. Chem.*, **38** (1946), p. 417.

(57) CONANT, F. S., LISKA, J. W.: *J. App. Phys.*, **15** (1944), p. 767.

(58) TUCKETT, R. F.: *Trans. Farad. Soc.*, **38** (1942), p. 310.

(59) WALL, F. T.: *J.A.C.S.*, **62** (1940), p. 803.

(60) UEBERREITER, K.: *Angew. Chemie.*, **53** (1940), p. 247.

(61) DAVIES, J. M., MILLER, R. F., BUSSE, W. F.: *J.A.C.S.*, **63** (1941), p. 361.

(62) BURGERS: *First Report on Viscosity and Plasticity* (Acad. of Sciences, Amsterdam, 1937).

(63) MARK, H.: *Cellulose and its Derivatives*, ed. E. Ott, p. 1025 (Interscience Publishers, New York, 1943).

(64) FLORY, P. J.: *Chem. Reviews*, **35** (1944), p. 51.

(65) TOBOLSKY, A., EYRING, H.: *J. Chem. Phys.*, **11** (1943), p. 125.

(66) REHNER, J.: *J. Polymer Sci.*, **1** (1946), p. 22.

(67) ZAPP, R. L., BALDWIN, F. P.: *Ind. Eng. Chem.*, **38** (1946), p. 948.

(68) ROBINSON, H. A., RUGGY, R., SLANTZ, E.: *J. App. Phys.*, **15** (1944), p. 343.

(69) TOBOLSKY, A. V., ANDREWS, R. P.: *J. Chem. Phys.*, **13** (1945), p. 3.

(70) STERN, M. D., TOBOLSKY, A. V.: *J. Chem. Phys.*, **14** (1946), p. 93.

(71) NUTTING, P. G.: *J. Frankl. Inst.*, **191** (1921), p. 679.

(72) SCOTT BLAIR, G. W., VEINOGLOU, B. C.: *The Sci. Instr.*, **21** (1944), p. 149; **191** (1921), p. 679.

(73) NUTTING, P. G.: *J. Frankl. Inst.*, **235** (1943), p. 513.

(74) HAWARD, R. N.: *Trans. Farad. Soc.*, **38** (1942), p. 394.

(75) PRESS, J. J.: *J. App. Phys.*, **14** (1943), p. 224.

(76) COUZENS, E. G., WEARMOUTH, W. G.: *J.S.C.I.*, **61** (1942), p. 69.

(77) BILMES, L.: *J.S.C.I.*, **63** (1944), p. 182.

(78) MOSIMANN, H.: *Helv. Chim. Acta*, **26** (1943), p. 369.

(79) CAMPBELL, H., JOHNSON, P.: *Trans. Farad. Soc.*, **40** (1944), p. 221.

(80) DOTY, P. M., ZIMM, B. H., MARK, H.: *J. Chem. Phys.*, **13** (1945) p. 159.

(81) GRALÉN, N.: *Dissertation Uppsala* (Almqvist & Wiksells, Uppsala, 1944.)

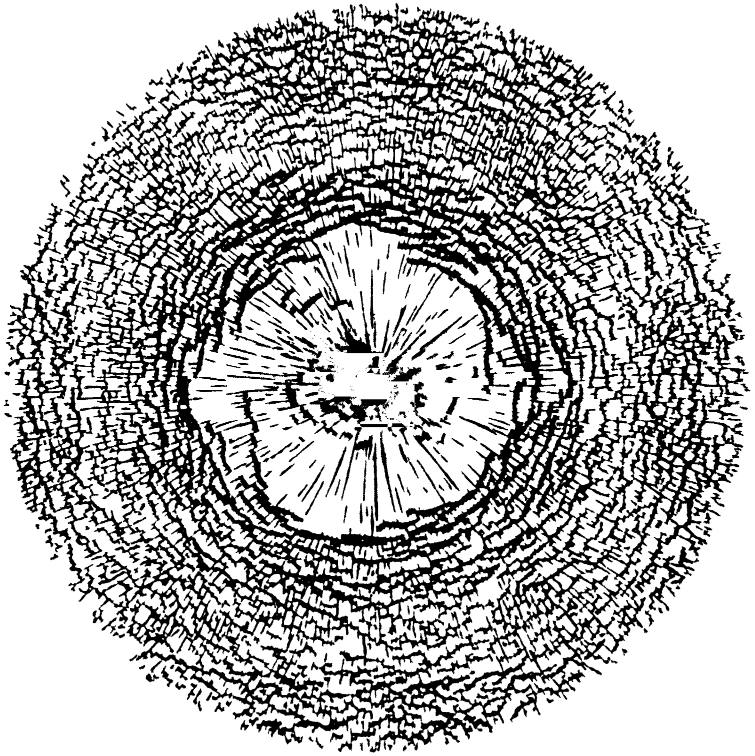
(82) HERMANS, J. J.: *J. Polymer Sci.*, **1** (1946), p. 233.

(83) POOLE, H. J.: *Trans. Farad. Soc.*, **21** (1925), p. 119.

(84) HAWARD, R. N.: *Trans. Farad. Soc.*, **39** (1943), p. 267.

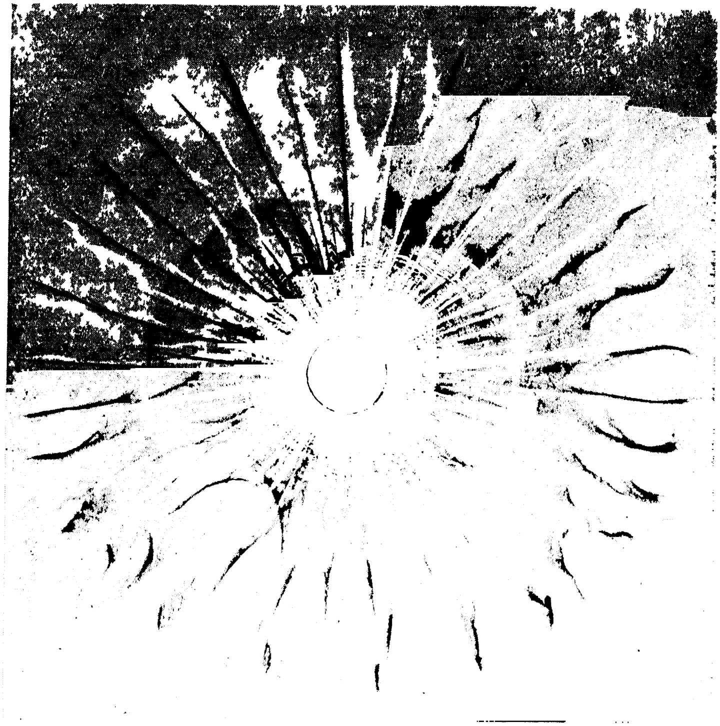
(85) PLUMB, D. S.: *Ind. Eng. Chem.*, **36** (1944), p. 1035.

PLATE I



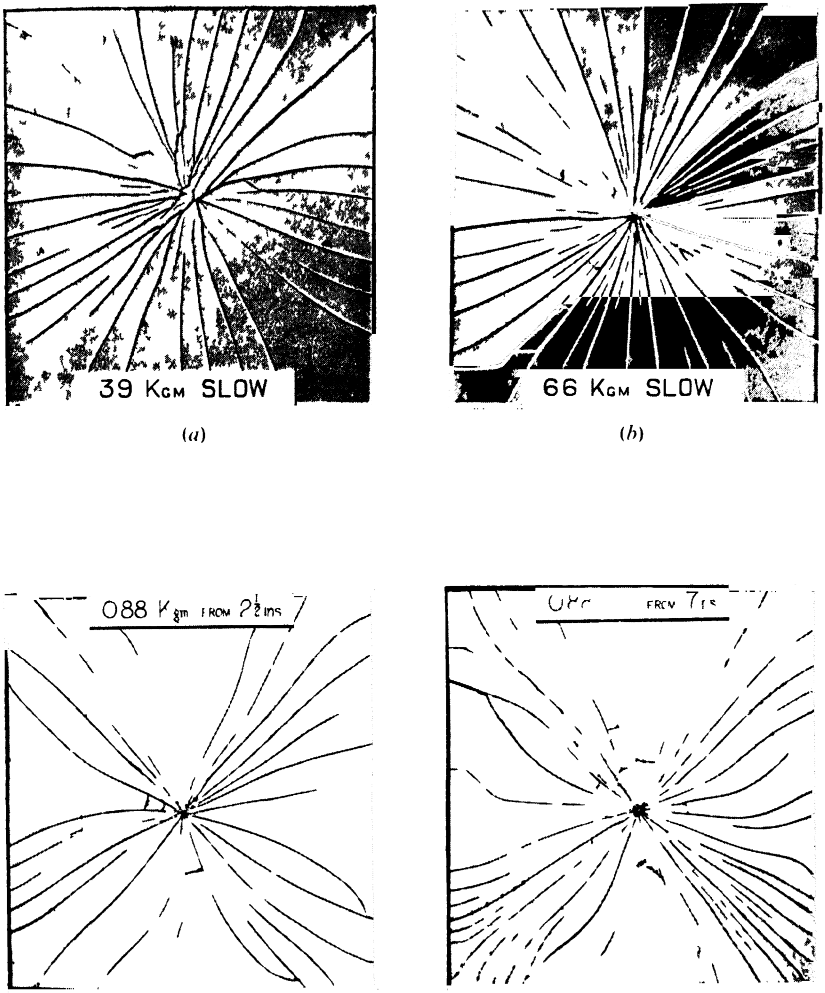
A spark photograph showing cracks spreading from the point of fracture in toughened glass Ref (66) Chap III

PLATE II



Cracks spreading from the point of fracture in plate glass
Ref (66) Chap III

PLATE III

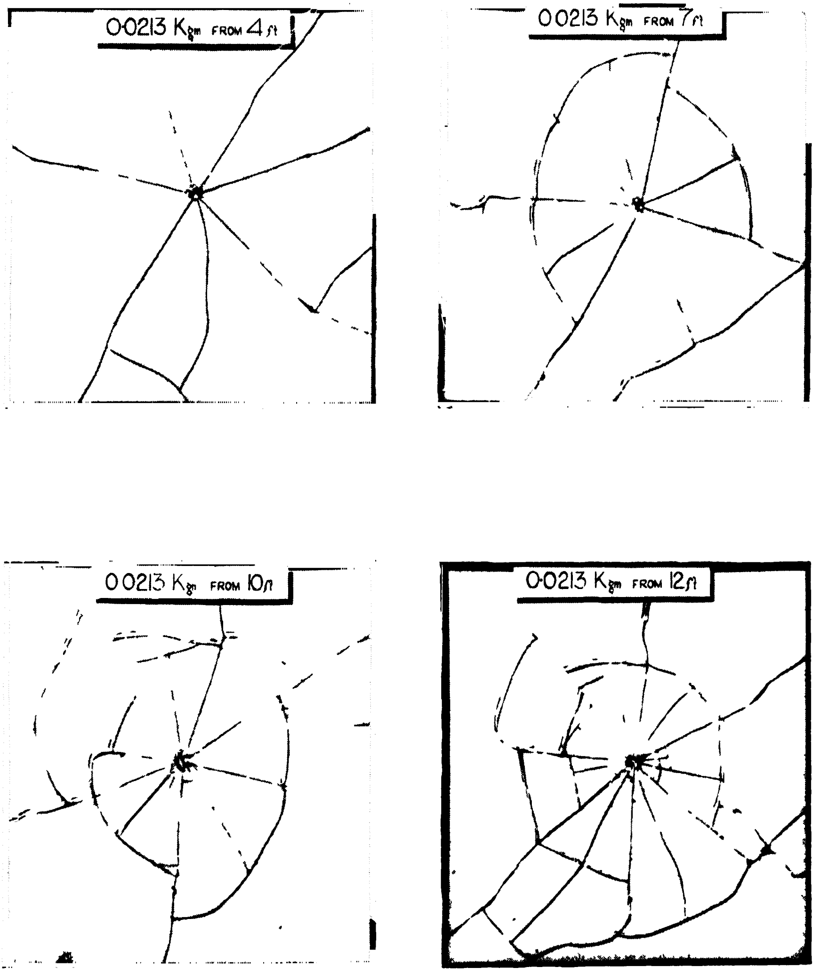


(a) (b)

(c) (d)

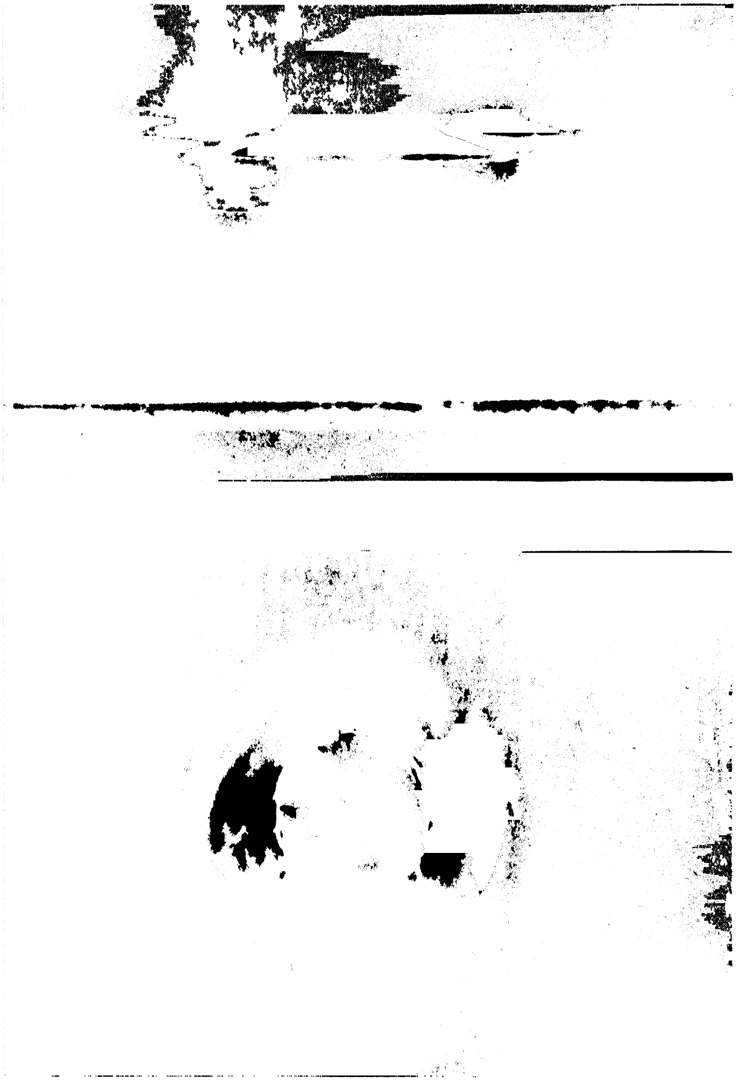
Fracture patterns in strong and weak squares of sheet glass under static bending (a and b) and low velocity impact (c and d) The stronger samples (b and d) show somewhat greater cracking Ref (16) Chap III

PLATE IV



The fracture of squares of sheet glass at medium velocities. In each case the blow was just sufficient to crack the glass. The types of pattern differ from those in static bending and low velocity impact, but the same tendency to increased cracking in the stronger samples may be observed. Ref. (16), Chap. III.

PLATE V



Hertzian cone fractures in glass Ref (12) Chap V

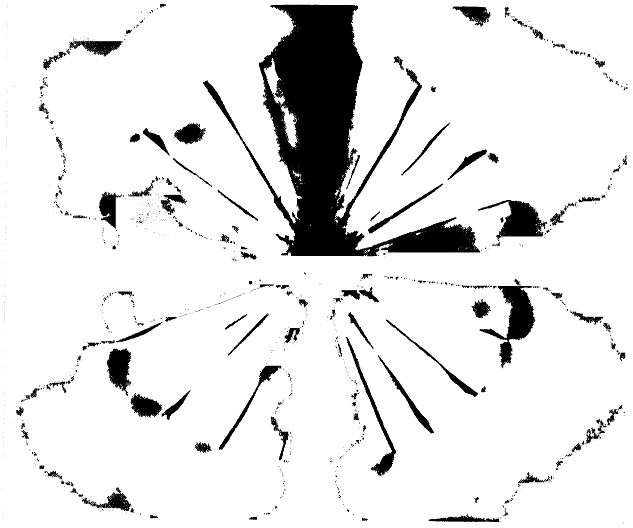
PLATE VI

The surface fractures formed when the hardness of glass is investigated by the rolling ball method Note the indication of "soft" patches in the glass
Ref (12), Chap V

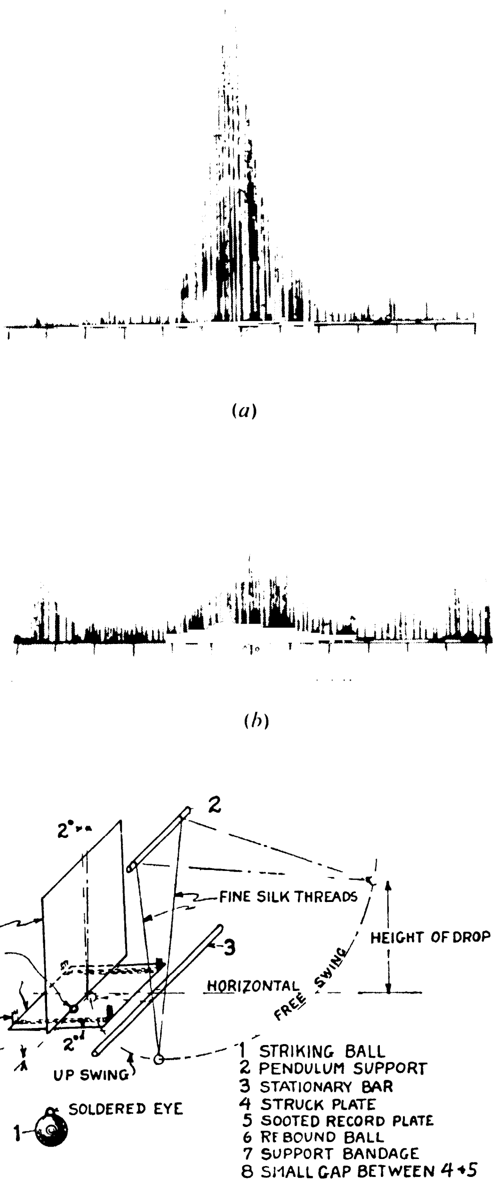
The Bierbaum scratching technique In this photograph the scratching tool is shown moved away to allow of microscopic examination of the scratch Ref (18), Chap V.

PLATE VIII

(*a*) The indentations given by the Vickers hardness tool (pyramid) and Bierbaum microcharacter Ref (18) Chap III

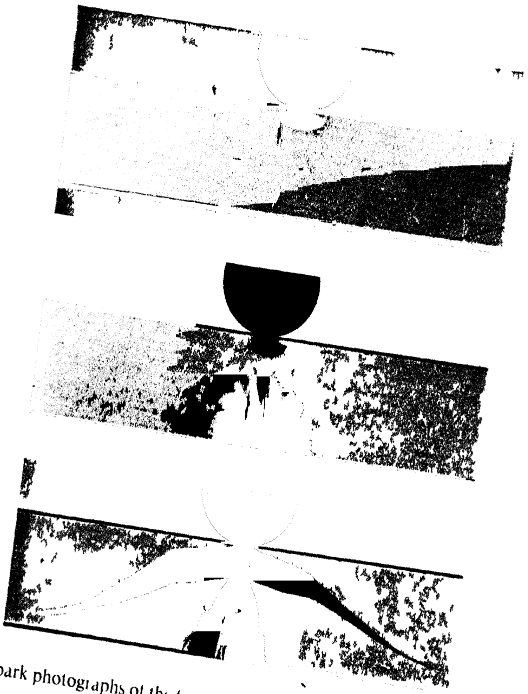


(*b*) The photoelastic stress pattern in plate glass during fracture. Ref (24), Chap VI

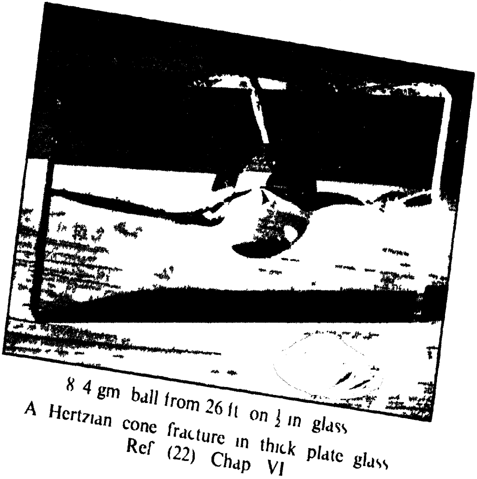


The falling ball arrangement for determining the impulse transmitted through a glass plate. Above, the trace given by (*a*) a steel and (*b*) an ivory ball. Ref. (26), Chap. VI.

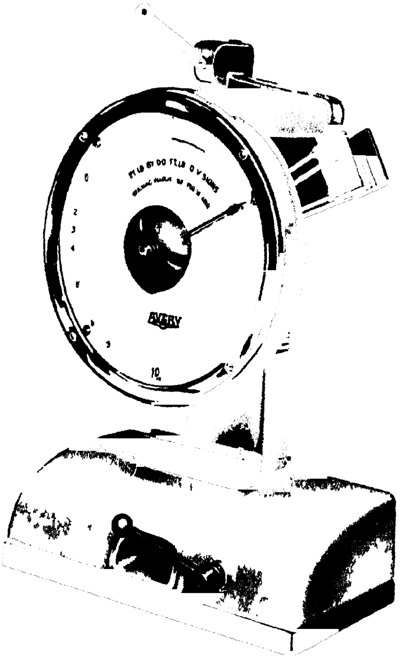
PLATE X



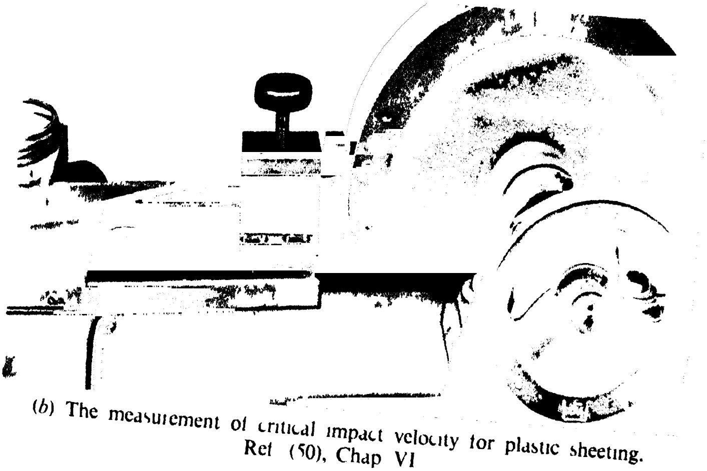
Spark photographs of the fracture process in a thick glass beam
Ref (66) Chap III



8 4 gm ball from 26 ft on ½ in glass
A Hertzian cone fracture in thick plate glass
Ref (22) Chap VI

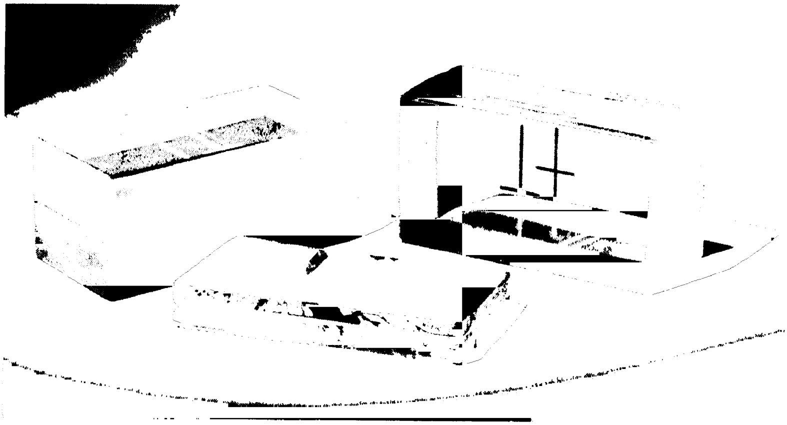


(*a*) A standard type of Izod impact machine (*Avery & Co Ltd*)

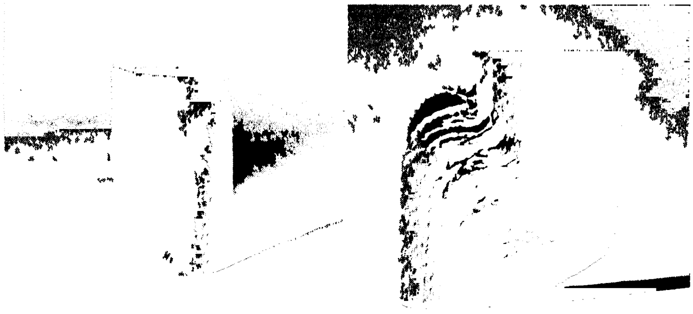


(*b*) The measurement of critical impact velocity for plastic sheeting. Ref (50), Chap VI

PLATE XII

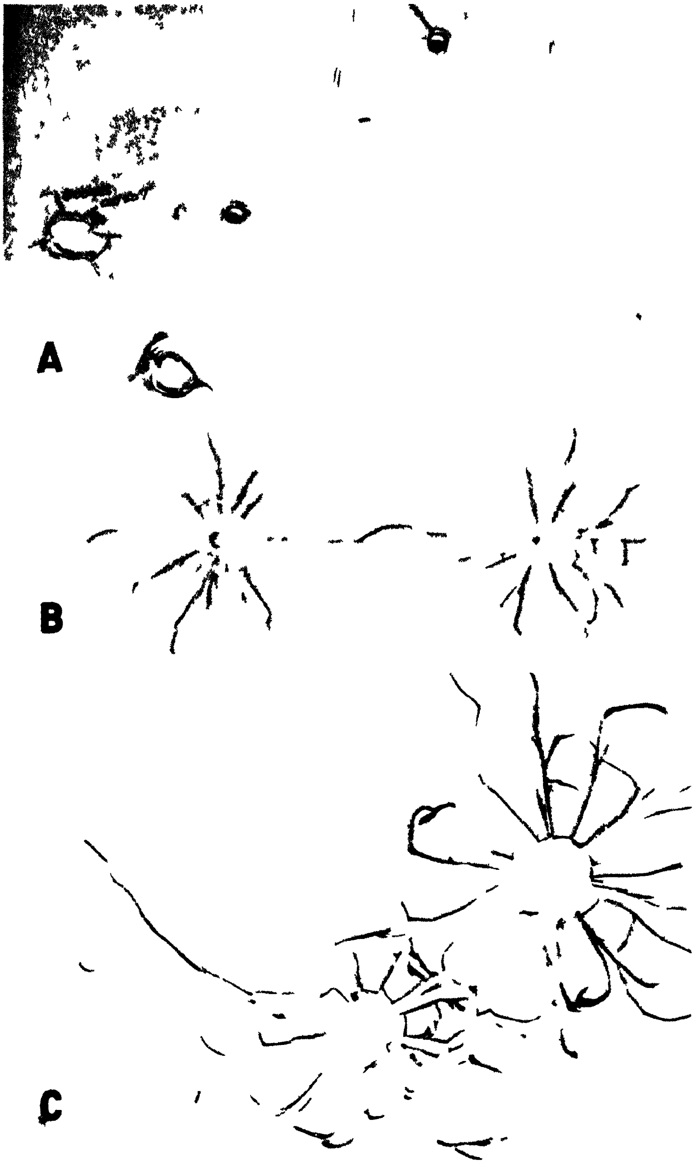


Bullet resisting windows used in tanks Bottom centre an armour piercing bullet fails to penetrate the last two layers of the block (*Colmore Adhesives Ltd*)



A shear fracture in compression with reinforced cresol resin
Ref (12), Chap VII

PLATE XIII



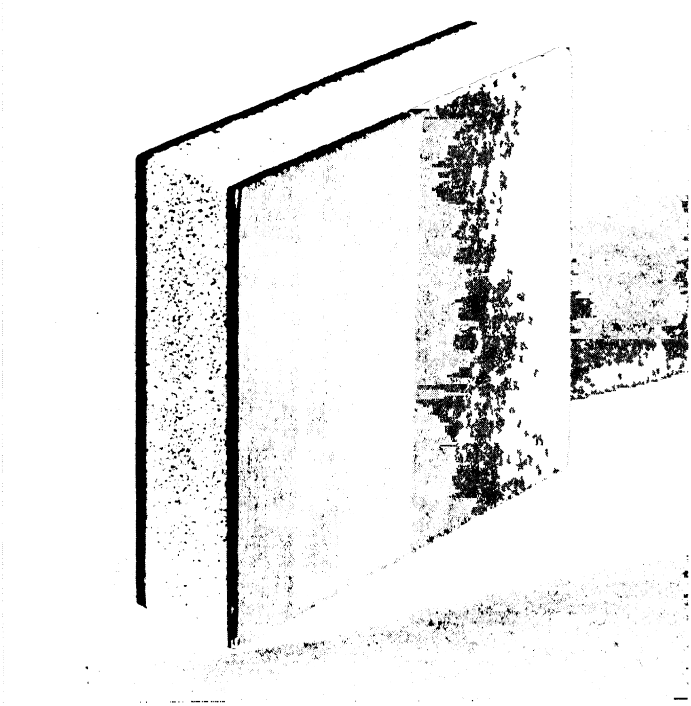
Effect of tracer bullets on transparent plastics Ref (32) Chap VI

(*A*) Cellulose acetate A2 0 095 in thick three tracer bullets calibre 30 at 100 yards one tracer bullet calibre 30 at 600 yards

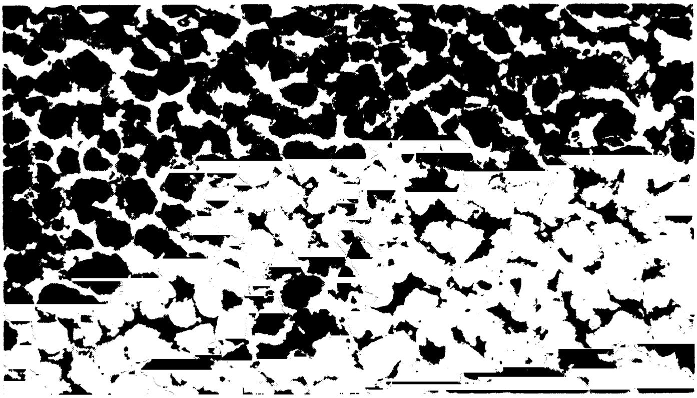
(*B*) Vinyl chloride-acetate resin, L3, 0 100 in thick, two tracer bullets calibre 30 at 100 yards

(*C*) Vinyl chloride-acetate resin L3, 0 100 in thick two tracer bullets calibre 50 at 100 yards

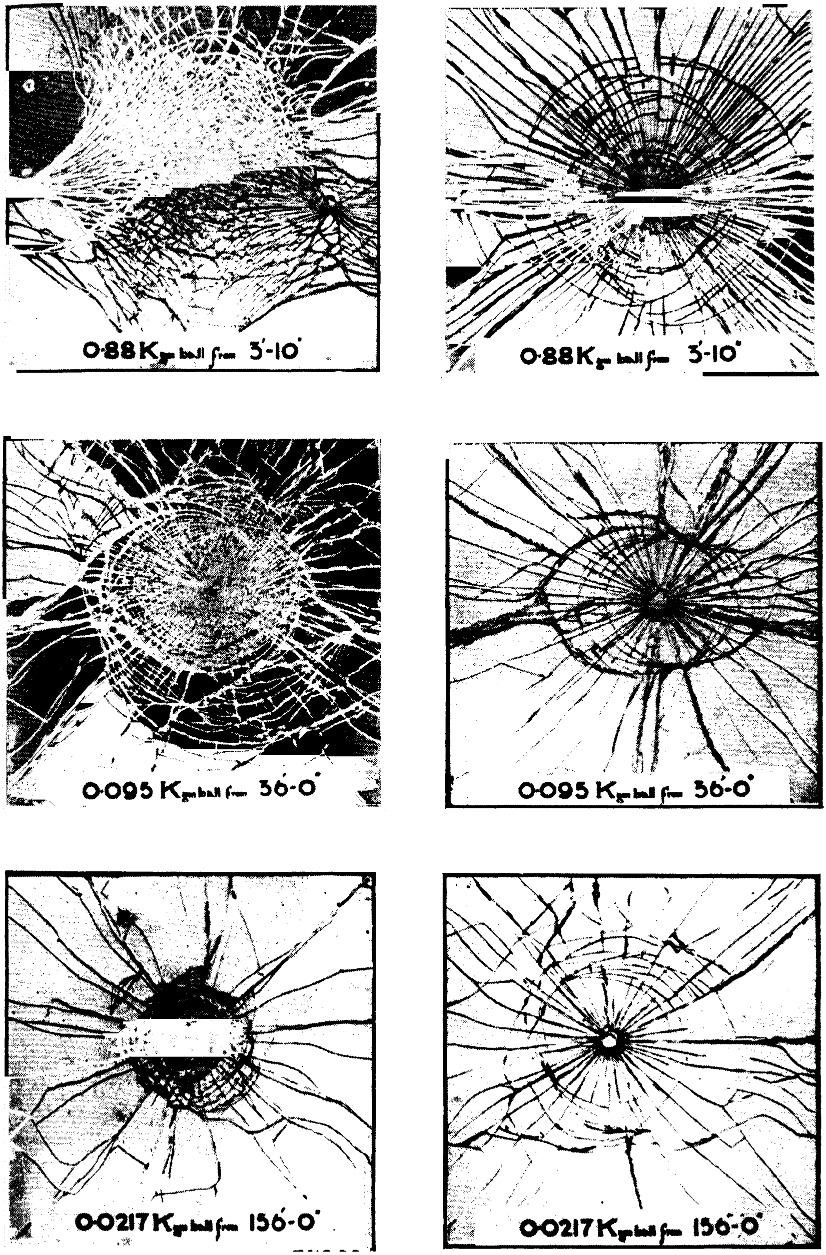
PLATE XIV



(*a*) Sandwich ebonite core faced with plywood

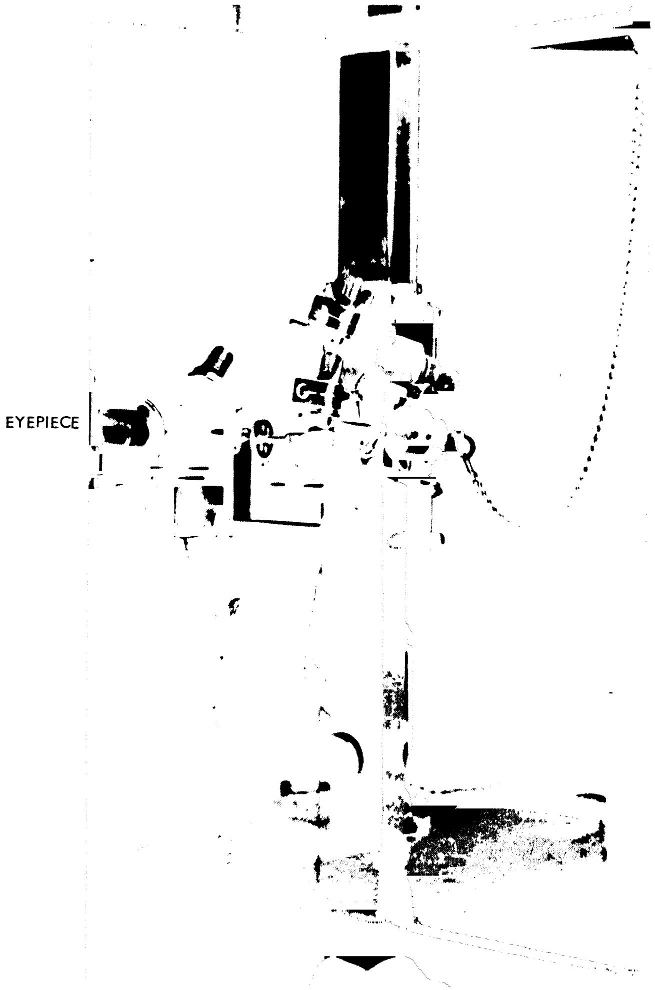


(*b*) Structure (10) of Plastazote, a typical expanded thermoplastic material (*Expanded Rubber Co Ltd*)


0·88 Kg. ball from 3'-10"
0·88 Kg. ball from 3'-10"
0·095 Kg. ball from 36'-0"
0·095 Kg. ball from 36'-0"
0·0217 Kg. ball from 156'-0"
0·0217 Kg. ball from 156'-0"

Fracture patterns in laminated glass with a cellulose acetate interlayer. As the velocity of impact (height of fall) is increased the cracking effects become more concentrated round the point of impact. Ref. (2), Chap. VII.

PLATE XVI



Apparatus for measuring the mechanical properties of fibre-glass. Ref. (30), Chap. IV.

(86) Hermans, P. H.: *Cellulosechemie*, **18** (1940), p. 97.
(87) Hermans, P. H.: *J. Phys. Chem.*, **45** (1941), p. 827.
(88) Hermans, P. H., Platzek, P.: *Kolloid-Z.*, **97** (1941), p. 329.
(89) Aiken, W., Alfrey, T., Janssen, A., Mark, H.: *J. Polymer Sci.*, **2** (1947), p. 178.
(90) Hermans, P. H.: *Kolloid-Z.*, **83** (1938), p. 71; Kratky, O., *Kolloid-Z.*, **64** (1933), p. 213; **68** (1934), p. 347; **70** (1935), p. 14; **84** (1938), p. 149.
(90*a*) Bunn, C. W.: *Advance in Colloid Science*, Vol. II, p. 124 (Interscience Publishers, 1946).
(90*b*) Gee, G. *Quarterly Reviews* (Chemical Society, London, 1947), **1**, p. 265.
(91) Meyer, K. H., Van Der Wyk, A. J. A.: *J. Polymer Res.*, **1** (1946), p. 49.
(92) Speakman, J. B.: *Nature*, **159** (1947), p. 338.
(93) Coker, E. G., Filon, L. N. G.: *Photoelasticity*, pp. 263–75 (Cambridge Univ. Press, 1931).
(94) Gurevich, G., Kobeko, P.: *Rubber Chem. and Tech.*, **13** (1940), p. 904.
(95) Church, H. F., Daynes, H. A.: *J. Res. Soc. Brit. Rubber Manfrs.*, **5** (1936), p. 11.
(96) Tuckett, R. F.: *Trans. Farad. Soc.*, **39** (1943), p. 163.
(97) Flory, P. J.: *J.A.C.S.*, **62** (1940), p. 1057.
(98) Morrison, G. O.: *Chem. and Ind.*, **60** (1941), p. 387.
(99) Treloar, L. R. G.: *Trans. Farad. Soc.*, **36** (1940), p. 538.
(100) Astbury, W. T.: *J. Soc. Chem. Ind.*, **64** (1945), p. 114.
(101) Tobolsky, Powell and Eyring: *The Chemistry of Large Molecules* (Interscience, 1943), p. 125; also Glasstone, Laidler and Eyring: *The Theory of Rate Processes* (McGraw-Hill, 1941).
(102) Sheppard, S. E., Carver, E. K., Sweet, S. S.: *Ind. Eng. Chem.*, **18** (1926), p. 76.
(103) Eley, D. D., Pepper, D. C.: *Nature*, **154** (1944), p. 52.
(104) Hazen, T.: *Mod. Plast.* (Oct. 1943), p. 103.
(105) Telfair, D., Carswell, T. S., Nason, H. K.: *Mod. Plast.* (Feb. 1944), p. 137.
(106) De Bruyne, N. A.: *Roy. Aero. Soc. J.*, **41** (1937), p. 523.
(107) Sutton, A. J.: *Brit. Elec. and Allied Ind. Res. Ass. Publication* B/T 37 (1943).
(108) B.S.S. 857 (1939).

CHAPTER V

HARDNESS AND RELATED SUBJECTS

AS will have been gathered from the introduction, no generally accepted and all-embracing definition of hardness exists. This chapter endeavours to deal with the general subject of hardness and related topics which are defined as the capacity of a surface of the material in question to remain unaltered in shape when subject to relatively concentrated mechanical forces which do not break the specimen as a whole. There are difficulties which must be taken into account in measuring or comparing the hardness of different solids, and under a concentrated force at least two separate groups of phenomena may occur.

Fracture Hardness.—The surface may be broken because the stresses set up exceed the breaking stresses of the material under the conditions of the test. If the point of loading moves this point of rupture may become a scratch.

Deformation Hardness.—The surface may merely be deformed by the forces operating. The deformations can be of any or all of the following types: (*a*) Irreversible; (*b*) Potentially reversible; (*c*) Reversible immediately or in the time allowed in the test.

Many measurements of hardness fall readily within one of these two groups, and then the precise relation of hardness to other mechanical properties must be worked out to allow for fracture if it is a significant item in the hardness measurement. However, sometimes, such as in the scratch hardness of plastics, it is not very easy to decide what part, if any, is played by the fracture of the surface. Further, in many cases, like transparent sheeting for aircraft, it is unimportant for practical purposes whether microscopic fracture or simple deformation takes place, but it is important to know if the surface is affected in its optical properties. Hence the practical value of methods based on the scattering of light from scratches and indentations which do not raise further questions, but any *theoretical* treatment must surely begin by raising just such questions.

A number of definitions of hardness have been used for metals, and these have been discussed by O'Neill,[1] who says that recoverable elastic deformations should be included when hardness measurements are based on an indentation technique. But a definition given by Hertz[2] treats hardness as essentially related to the irreversible phenomena occurring when the "yield point" of the material is exceeded in any part of the stress system. It is not intended to attempt further limitation of the term hardness here, but rather to deal with a number of measurements falling within its scope as defined at the beginning of this section.

Forces Surrounding a Spherical Body in Contact with a Plane Surface

The theory put forward by Hertz[3] and Fuchs[4] to describe the forces surrounding two spherical bodies in contact is fundamental to the whole problem of hardness. For the theoretical treatment and derivation of the fundamental relations the reader is referred to Timoshenko,[5] and Love,[6] and we shall simply detail here the relations applying in the special case when one of the spheres concerned is of infinite radius, i.e. a plane surface, and the other of radius r.

The suffixes to E and σ in the formula refer to the elastic properties of the two materials involved.

If the sphere is subject to a normal load P its centre will approach the plane by a distance x, and it will be in contact with the plane in a circle of radius a where these quantities are determined by the following relations:

$$a = \sqrt[3]{\frac{3}{4} P r \left[\frac{(1-\sigma_1^2)}{E_1} + \frac{(1-\sigma_2^2)}{E_2}\right]}$$

$$x = \sqrt[3]{\frac{9}{16} \frac{P^2}{r} \left[\frac{(1-\sigma_1^2)}{E_1} + \frac{(1-\sigma_2^2)}{E_2}\right]^2}$$

$$q_0 = \frac{3}{2} \frac{P}{\pi a^2}$$

where q_0 is the maximum pressure at the centre of the circle of contact.

A general picture of the distribution of these forces is given in Fig. 56,[6] where the principal lines of force are shown.

The maximum shearing stress is below the centre of the circle of contact and is equal to $0 \cdot 31\, q_0$ (when $\sigma \sim 0 \cdot 3$), and the maximum tensile stress is at the edge of the circle of contact and is given by

$$\text{The maximum tensile stress} = \frac{(1 - 2\sigma)}{3} q,$$

In the case of a glass with $\sigma = 0 \cdot 25$ this maximum tensile stress $= 1/6\, q_0$. Here the value of σ applies to the material in which the stress is being estimated.

Application of the Hertzian Equations to Glass

In order to test the validity of the above relations, Auerbach[7] made a series of experiments on the contact of spherical glass lenses with a plane surface. In these investigations he attempted to relate both deformation and fracture properties with the Hertzian theory. In the deformation experiments he pressed a lens of known curvature against a polished surface of the same glass and measured the diameter of the circle of contact by microscopic examination. The results with a particular lens gave a constant value P/a^3, and with different lenses of the same glass P/a^3 was also constant within the experimental error for lenses of different radii. From these figures Auerbach concluded that the equations of Hertz were obeyed and went on to determine the quantity $E/(1 - \sigma^2)$. From it he was able to list values of σ for different glasses using the known values of the Young's modulus. However, his results did not agree with those of Straubel, though this is not altogether surprising since a small error in $(1 - \sigma^2)$ will inevitably lead to larger errors in σ. These were estimated by Auerbach as of the order of ± 7 per cent; presumably this estimate is too low.

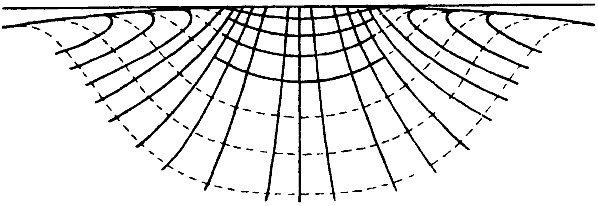


FIG. 56.—The principal lines of force in a sphere in contact with a plane.[6]

Auerbach went on to make experiments on the breaking of glass under these conditions by increasing the pressure until a ring crack or Hertzian cone fracture (Plate V) was formed round the circle of contact. On the average he found that these cracks were 19 per cent larger than the circle of contact. Using the same type of glass with different lens radii, he investigated the relation between the force P' required to produce the ring fracture and the lens radius. As a result he found that the quantity P'/r remained approximately constant for the different values of r and was characteristic of the glass used.

Now if in these experiments glass were breaking under a uniform tensile stress, then q_0 should be constant, i.e. $\sqrt[3]{P'/r^2}$ should be a constant. Obviously this is not the case. We now know that this "anomaly" is a consequence of the size factors involved in the tensile strength of glass. However, Auerbach proceeded to examine the question of hardness in relation to the possible constant quantities which did conform with his experiments for particular glasses, and reached the conclusion that the hardness of a glass was best measured by the particular constant quantity which has since been called the Auerbach hardness,

where: $$\text{Auerbach hardness} = q_0 \sqrt[3]{r} = H$$

He considered this quantity was best suited to represent the hardness of glass, but was able to establish only a very rough relationship between it and the results of scratching experiments.

This work represented a very complete attempt to evaluate the fracture hardness of a material in terms of theoretically understood properties, though the constants obtained did not correspond with what was then expected as a consequence of the Hertz equations. Subsequently, therefore, the general subject of ring cracks was widely discussed. For instance, Raman[8] showed that they could be formed dynamically by allowing a polished steel ball to fall on a thick glass plate. The question has been discussed theoretically by Preston,[9] who concluded, firstly, in general agreement with Auerbach, that the cracks developed from a point where the glass surface was subject to tension only and therefore did not justify the view that glass could be broken under other types of stress, and secondly, that the apparent failure of the Hertz relations was due to the glass breaking from nuclei or weak points and the consequent dependence of strength on the scale of the experiment. According to this view the whole phenomenon is simply a particular aspect of the area-strength relation

(Chap. III), and the constancy of P'/r discovered by Auerbach is a casual outcome of the particular form of flaw distribution operative under his conditions.

Thus in the light of present knowledge Auerbach's experiments should be regarded as demonstrating the increase in the tensile stresses required to rupture glass which takes place as the scale of the experiment is reduced. These phenomena have recently been further investigated by Preston,[10] who estimated the maximum tensile stress, according to the Hertzian formula, which was required to fracture glass in contact with loaded balls of differing diameter. His results (Table XXIII) show that with small balls fracture strengths comparable to glass fibres are obtained. While Preston's results generally agree with Auerbach concerning the high fracture stresses observed, they would not fit Auerbach's formula accurately.

TABLE XXIII. THE MICRO STRENGTH OF GLASS AS A FUNCTION OF BALL DIAMETER AND SURFACE TREATMENT

Ball diameter *D*	Sample	Surface	Average load	Cone *d*	Maximum stress	Maximum stress
in.			lb	average in	lb./in.²	kg /cm ²
0·020	⅛ in. F	Unetched	18·2	0·0066	235,000	16,500
0·031	⅛ in. F	Unetched	30·8	0·0082	209,000	14,700
0·031	⅛ in. F	Etched	30·7	0·0083	208,000	14,600
0·039	⅛ in. F	Unetched	36·4	0·0101	188,000	13,300
0·039	⅛ in. F	Etched	62·1	0·0109	223,000	15,700
0·063	⅛ in. F	Unetched	36·2	0·0123	138,000	9,700
0·063	⅛ in. F	Etched	58·4	0·0127	163,000	11,500
0·125	5/16 in. P	Etched	54·5	0·0190	100,000	7,000
0·250	5/16 in. P	Etched	76·5	0·0260	71,000	5,000
0·500	1 in. P	Unetched	113·0	0·0330	53,000	3,730
1·00	1 in. P	Unetched	226·0	0·0520	40,000	2,820
1·25	1 in. P	Unetched	377·0	0·0712	41,000	2,890

Here F stands for Fourcault and P for plate glass.

From all this work it is to be expected that as the scale of the experiment is reduced, beyond the existing limits obtained with 0·020 in. balls, very high fracture stresses will be required, a property which accounts for the characteristic permanence of a glass surface and, in particular, its relative capacity to resist damage by sharp points which injure other materials. In the case of toughened glass the above considerations allow of a further development when taken together with the theory of that material

(Chap. III). There it was suggested that the strength of toughened glass was due to a surface compression which had to be overcome before the glass could be broken in tension. Further, the measured figures suggest (Table X) that this surface stress is commonly of the order of 1,000 to 2,000 kg./cm.^{2} Now although this involves a tremendous increase in the ordinary bending strength of glass, it represents, on the basis given, only a relatively slight improvement in relation to the stresses occurring under highly concentrated loads. Hence the resistance of toughened glass to scratching and similar treatment should not show a great improvement on untoughened material of similar composition. This conclusion is supported by the well-known fact that toughened glass is readily shattered by tapping it with a centre punch, i.e. subjecting it to a concentrated load. Further, the experiments carried out by Holland and Turner on the scratch resistance of toughened glass and plate glass,[11] in which a number of different scratching agents were used, indicate that the differences in behaviour between the two materials are not large. Some results taken from one of their groups of experiments are presented in Table XXIV.

TABLE XXIV. WIDTH OF SCRATCH PRODUCED BY CONICALLY GROUND AND POLISHED DIAMOND UNDER CONSTANT LOADING CONDITIONS ON ORDINARY PLATE AND TOUGHENED PLATE GLASS

Sample No.	Width of scratch in cm $\times 10^{-4}$	
	Near centre of sheet	Near edge of sheet
Toughened A1 (*a*)	8·8	6·0
Toughened B1 (*a*)	7·8	6·5
Ordinary plate (*a*)	8·8	8·8
Ordinary plate (*b*)	8·6	8·6

The diminution in scratch thickness near the edge with toughened glass is noted by Holland and Turner as a characteristic property.

The investigations of ring cracks in relation to hardness has been further pursued by Bailey[12] (Plate VI). He set up an apparatus whereby a $\frac{1}{8}$-in. ball could be rolled over the glass under an increasing load, and took the value of the load in lb., corresponding to the point where fracture began, as a measure of hardness. His ball tracks gave very variable results with fire-finished surfaces and seemed to indicate the existence of soft areas in the glass.

The results obtained yielded high values for fire-polished Fourcault sheet (25 to 28) and a microscopic slide (29 to 34), a medium value for polished plate (21 to 23), and low values for borosilicate (16 to 20) and fused silica (10·5 to 16·8). These differ from the results of Auerbach, who obtained a high value for quartz. However, the compositions of the glasses giving Auerbach's low hardness values differed largely from those on which the more recent experiments have been carried out, and the differences may therefore be more apparent than real. Bailey's results differed also from those of other workers. To explain the difference between his results and those given in grinding tests Bailey suggests that with quartz and borosilicate (pyrex) glasses a scratch is more easily formed but does not spread subsequently as in the conventional window glass, so the energy required to grind the glass away remains large. A further point mentioned by Bailey is that in scratching tests high temperatures may occur locally, as shown by sparks, and such conditions will favour high melting-point glasses like silica and pyrex. Finally, Bailey concluded that since small fractures easily deteriorate under weathering, and are in any case surrounded by wider regions of strain, it is the formation of the initial surface fracture which is the most vital service property affecting the hardness of glass.

Measurements Applicable to Plastics and Glass

The above methods are applicable to glass but not to most plastic materials. For instance, under a concentrated load applied by a hard ball plastics are seldom broken at the point of loading and generally suffer deformation alone. Thus the application of such loads leads to measurements of the deformation, which may be in practice, but are certainly not in theory, comparable with the result obtained with glass. Nevertheless, for many purposes it is important to be able to compare the scratch resistance of plastic materials with other plastics and with glass, and in particular to measure the optical properties before and after a specified treatment. To deal with this problem two types of test have been used, namely, the *mar-resistance* test, in which an abrasive is allowed to fall on the surface of the material, and the *scratch test*, where a sharp implement is caused to move across the surface under specified conditions. The first is more suitable for comparing plastic and glass, since the same abrasive can be used for each material and there is not the difficulty of defining the edge of a scratch that there is with most glasses. Each of these tests avoids raising the question of the distinction between fracture and deformation. It is possible that this confusion is essential in any method which aims at comparing the behaviour of glass and plastics directly.

Abrasion Hardness of Plastics and Glass

An abrasion test capable of use with both plastics and glass has been described by Starkie,[13] who used it to compare the scratch resistance of cellulose plastics, perspex (methacrylate) sheet and glass. He considered that this type of test was superior to a scratch test for making reproducible and comparable measurements with varied materials.

TABLE XXV. ABRASION RESISTANCE OF PLASTICS AND GLASS

Material	Abrasion resistance No
Polystyrene	12·1
"Perspex" (methacrylate) transparent resin sheet	17·6
Cellulose acetate	20·6
Celluloid film base	21·8
Unplasticized "Perspex" (methacrylate)	30
Glass microscopic slide	111·3
Common sheet glass	115·5
Polished plate glass	131·3
Pyrex glass	183·2

In this method (Fig. 57) the specimen is placed on a hinged support so that in one position it could be subjected to a stream of falling carborundum particles, and in the other position it is illuminated by a parallel beam of light. Directly opposite the test piece in the latter position a calibrated photo-electric cell is placed with an opaque disc in the centre so that only light scattered by the abraded material is recorded. After abrading the specimen under standard conditions and replacing it in the position for measurement, an increase *d* in the galvanometer reading is observed and the scratch resistance is measured by the arbitrary quantity 1,000/*d*. The standard conditions for abrasion allow 40 gm. of a carborundum, which would just pass through a 60-mesh sieve, to fall down the 2-ft. tube on to the specimen inclined at 30° to the vertical, so that the particles bounce away and do not fall a second time on to the point of abrasion. Results obtained in this way are given in Table XXV.

The occurrence of markedly higher values for the scratch resistance of glass compared with those of the plastics is only to be expected, but the differences within each group are interesting. The glass results may be compared with those from a somewhat similar method used by Milligan,[14] in which the number of blasts from a sand blast nozzle required to give a standard penetration

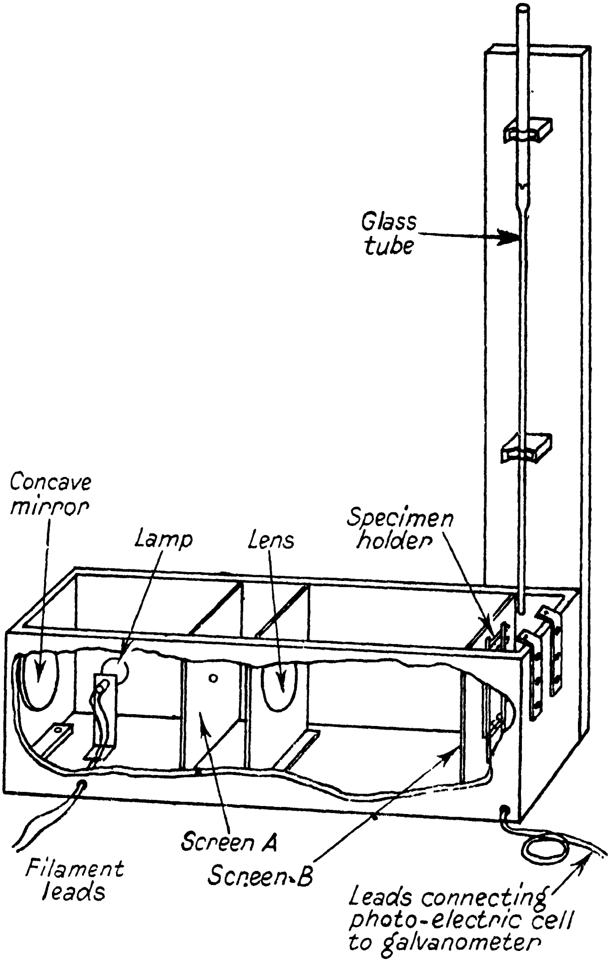


FIG. 57.—An apparatus for measuring the abrasion or mar-resistance of plastics or glass.[13]

of the glass was measured. Here also, pyrex was found to give higher results than other types of glass except silica, which required 3·5 to 3·8 times the number of blasts for a standard plate glass. Other somewhat similar experiments, in which glass rods were ground against a steel plate with powdered quartz abrasive, have been described by Scholes.[15] He also found that silica glass was the most resistant to abrasion and concluded that this was due to the silica. Boric oxide was much less effective than silica in supplying hardness, but when boric oxide replaced lime the glass became less abradable. The substitution of lime for soda in a sodium silicate had little effect. In general Scholes agreed with Milligan in finding that most common commercial glasses were about three times as abradable as pure silica, and with Starkie in finding that pyrex glass was appreciably harder than other commercial types, which Scholes attributed to its high silica and low alkali content.

The methods of Starkie were largely reproduced in the simultaneous work of Boor[16] in the U.S.A., who worked on plastic materials and also rejected the scratch type of test, giving as his reasons lack of accuracy and disagreement with service experience. The method used, which is generally similar to that of A.S.T.M. D 673—42 T,[17] has several similarities to Starkie's apparatus, such as a fall for the abrasive of 25 in. (24 in.) and the setting of the specimen at 45° (30°) to the vertical. The results are construed in terms of the percentage of the original gloss remaining after abrasion, i.e. the reduction in reflection rather than the increase in scattering.* Boor found that slightly different results are obtained according to whether a method of averaging a number of results using large and small quantities of abrasive, or a single measurement with a small quantity, was used. Results from different laboratories employing the same specification were not in complete agreement where small differences between different materials were concerned, but all agreed in putting the urea melamine laminate first, cellulose acetate second, and polystyrene last in order of scratch resistance among the materials tested. On the other hand, the results showed little correlation with those obtained from the Bierbaum scratch apparatus. Boor used the term "mar-resistance" to describe the property which he was seeking to measure, and distinguished between this and other properties covered by the term hardness, such as resistance to compression and indentation. Some of his results are summarized in Table XXVI; but the two columns given here do not include the experiments with window glass, which was found to be more resistant to abrasion than any of the plastic materials, though the advantage over the urea melanine laminate was relatively small according to this method of measurement. The difference in the relative values given to methacrylate and cellulose acetate by Starkie and Boor could be due to differences, such as a difference in plasticization, in the materials tested.

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* This allows of application to opaque materials.

TABLE XXVI. THE "MAR-RESISTANCE" OF PLASTICS
(After Boor)

Material	Average of abrasion experiments	Rating	Bierbaum micro-character	Rating
Urea-melanine laminate ..	76·9	1	30·9	2
Cellulose acetate	69·2	2	12·2	6
Vinylite	60·1	3	12·2	7
Urea-thio-urea laminate ..	59·4	4	21·4	3
Methacrylate	57·0	5	21·4	4
Phenol formaldehyde laminate	52·8	6	47·6	1
Polystyrene	32·7	7	15·8	5

Scratch Hardness of Plastics and Glass

Although the experiments of Starkie and Boor have the advantage of giving readily comparable results for numerous types of plastics and for glass, and appear to overcome a difficulty mentioned by Kline and Axilrod[18] in that the use of a sieved abrasive overcomes a polishing tendency caused by the finer fragments, there is at present no full agreement on the advantages of the abrasion method with plastics. Numbers of results for scratch hardness have been submitted in which the impression of a moving diamond tool on a plastic surface is measured and a high degree of accuracy claimed. For such a purpose a number of types of sclerometer are already available in metallurgy, and their various applications have been discussed by O'Neill.[1] For plastics, Kline and Axilrod[18] used the Bierbaum "micro-character" scratch resistance apparatus (Plate VII); the plastic specimen is attached to a screw arrangement so that the diamond point can be steadily moved over the surface, leaving a mark whose width is conveniently measured with a microscope. The diamond used has the form of the corner of a cube and is held down by a 3-gm. weight. The scratch hardness is then given by the load in kg. divided by the square of the scratch width in mm., and is shown to be largely independent of the thickness of the sheet used. Some of these results are given in Table XXVII, where they are compared with a Vickers indentation hardness test.

Table XXVII. Scratch Resistance and Indentation Hardness of Various Plastics

Material		Thickness	Scratch No	Vickers hardness
		mil	kg./cm^2	kg./cm.^{2}
Cellulose acetate	1	63	8·2	7·9
	1	62	8·2	6·8
	2	56	7·4	5·6
	2	95	7·3	5·5
	2	125	7·5	5·2
	3	64	9·9	6·9
	3	95	11·9	7·7
	3	133	10·1	7·1
	4	162	5·3	7·0
Cellulose nitrate	1	67	9·9	11·6
	2	64	10·0	10·5
Ethyl cellulose	1	57	5·5	5·6
	2	29	6·3	6·7
Acrylate resin	1	116	15·0	13·6
	2	66	15·0	15·4
Vinyl resin	1	56	10·2	15·3
Styrene	1	79	10·5	19·8

These figures are of interest because they confirm Starkie's view that the acrylate sheets give better results than cellulose acetate, but here the styrene is given a comparatively high rating. However, in comparing results of this nature it must be remembered that names like "cellulose acetate sheet" can cover a range of materials with very different properties. In three cases the figures appear to be close to those given by an indentation hardness deformation test, but with styrene and the vinyl resin the scratch figures are relatively lower than those from deformation experiments. The marks given by the two types of instrument are illustrated in Plate VIII(*a*).

The value of the scratch method is contested by Starkie, who put forward evidence that the results depend on the velocity of scratching; he also considered they were excessively erratic and insensitive with light loads. Nevertheless, he investigated the scratch method, and in particular the dependence of scratch width on load, and showed that the relation, scratch width — $\sqrt{\text{load}}$, was linear for loads of 25 to 625 gm., but that with heavier loads somewhat wider marks were obtained than the theory would predict. Curves showing the effect of load and scratch velocity are also given by Perkuhn[19] (Figs. 58 and 59). For measurements of scratch hardness Perkuhn used an electric motor to give a standard velocity of 0·3 mm./sec., and estimated the hardness by the relation

$$H = \frac{8P}{b^2} \sin\frac{\Theta}{2}$$

where P is load, b is width of scratch, and Θ the included angle of the diamond tool. However, the figures obtained for H are not independent of load by this method but become approximately so for loads of 30 to 100 gm. (Fig. 60). It is claimed that individual measurements are reproducible to within $\pm$ 1 per cent.

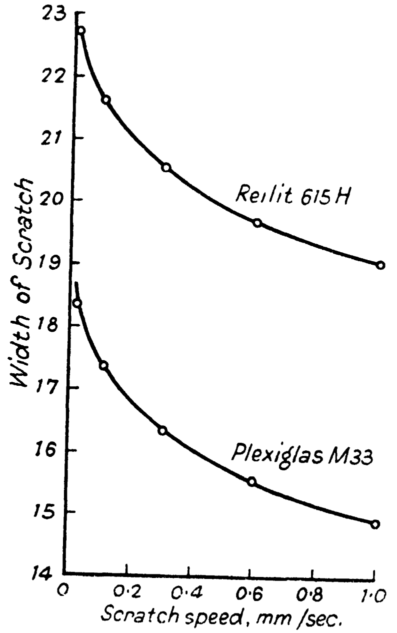


FIG. 58.—The relation between the width of a scratch and the rate of scratching.[19]

Reilit 615H is cellulose triacetate and Plexiglas M.33 is polymethyl methacrylate.

His values again give relatively high ratings for the acrylate (Plexiglass) plastics and also show an interesting correlation between scratch hardness and tensile strength for similar materials at different temperatures (Table XXVIII).

In the present circumstances it is not easy to correlate the results obtained by different workers using different methods, owing to the uncertainty of the material used and the actual effects obtained. Clearly, both scratch and abrasion methods have a common characteristic in that ideal Hookean deformations are not directly measured, i.e. they do not include the deformation while under load, as recommended by O'Neill for metals.

TABLE XXVIII. SCRATCH HARDNESS IN RELATION TO TENSILE STRENGTH AND TEMPERATURE

Material	Temperature	Scratch width	Scratch* hardness	Tensile strength	Tensile strength / Hardness	Tensile strength / Hardness (mean value)
	° C.		kg./cm.²	kg./cm.²†		
Plexiglass M222	4	14·6	10·300	900	0·087	0·087
	20	15·2	9·559	820	0·086	
	40	17·1	7·550	660	0·087	
Plexiglass M132	4	15·8	8·830	760	0·086	
	20	17·0	7·630	675	0·087	
	40	19·0	6·100	540	0·088	
Plexiglass M33	4	15·4	9·300	800	0·086	
	20	16·4	8·210	720	0·087	
	40	18·6	6·370	560	0·088	
Reilit	4	19·7	5·670	650	0·114	0·113
	20	20·6	5·200	595	0·111	
	40	22·0	4·550	520	0·114	
Astralon .. (polyvinyl chloride)	4	21·5	4·770	760	0·159	0·157
	20	22·8	4·250	660	0·155	
	40	27·6	2·890	460	0·159	

* A 10-gm. load was used in this case.
† Determined for loading rate of 300 kg /cm.²/min.

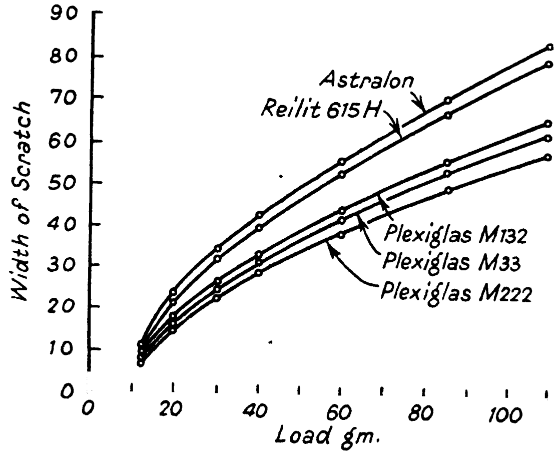


FIG. 59.—The relation between the scratch width and the load on the scratching tool.[19]

However, in this they are justified by their specific purpose and the simulation of the conditions of use.

Scratch hardness in glass has been investigated by Gehlhoff and Thomas[20] as a function of composition, using their usual method of replacing SiO_2 separately by various basic oxides. Mostly, their results show that addition of up to 10 per cent of the basic oxide causes an increase in scratch hardness, but that subsequent additions cause a decrease (K_2O, Na_2O, B_2O_3), cause a further increase (MgO, CaO, ZnO, BaO, Al_2O_3), or have little effect (Fe_2O_3, PbO). The conditions of testing used were such that a cubic diamond was subjected to a load of 20 gm. and the width of the scratched measured. This was always found to be between the extreme values of 0·0039 to 0·0091 mm., i.e. the total differences with different glasses were not large. Using the

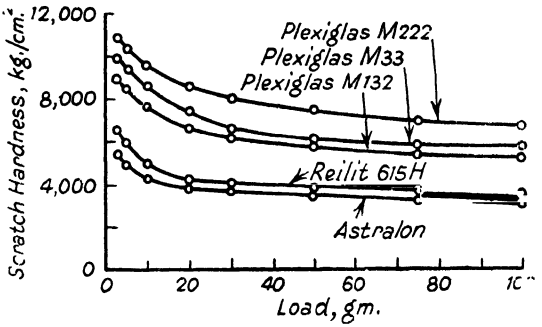


FIG. 60.—The relation between the scratch hardness as determined by Perkuhn and the load.[19]

formula quoted by Perkuhn, this yields hardness figures of 740,000 to 135,000 kg./cm.,^{2} i.e. this method of measurement gives a far larger difference between plastics and glass than the abrasion experiments. Their results also apparently differ from those of Milligan[14] and Starkie,[13] but rather agree with those of Bailey[12] in that the results for silica are not exceptionally high compared with glasses containing basic oxides, but, again, precisely the same materials may not have been investigated in each case. The apparent contradictions obtained in these tests illustrate the complexity of the hardness problem even in approximately similar circumstances. At present it is not easy to say how far these differences lie in the methods used and how far in the materials tested, and, accordingly, it appears inevitable that for some time to come the capacity of a surface to resist visual damage will have to be measured by methods based solely on the direct simulation of service conditions.

Measurements of the Indentation Hardness of Plastics

In this type of hardness measurement a concentrated load is applied to the plastic and the impression or penetration so produced is recorded. A variety of procedures have been used, of which four typical cases are very briefly described below.

Brinell Hardness.—A hardened steel ball, about 2·5 mm. in diameter, is pressed into the smooth surface of a plastic material under a pressure of 25 kg. for about 30 sec. The size of the indentation is measured by a microscope, and the hardness number is obtained by dividing the spherical area into the pressure applied. A temperature of 68° F. has been recommended for test purposes.[21]

Rockwell Hardness.—A ¼-in diameter ball penetrator is placed under a minor load of 10 kg. and then a major load of 100 kg. applied in 6 to 8 sec. and removed in 1 sec. A penetration indicator shows the amount of deformation which has taken place, and the reading on an arbitrary inverse scale is based on the difference between the penetration under the minor load before and after the major load has been applied. The test is very convenient and a number of variations are possible; the one described is the Rockwell M scale.[22]

Vickers Pyramid Test.—This has been described by Kline and Axilrod,[18] who used a Vickers testing machine. A square pyramid having an angle of 136° between opposite faces is pressed for 10 sec. into the specimen. The length of the diagonal impressions (Plate VIII) are then measured microscopically and the Vickers number is the quotient of the applied load to the pyramidal area. Kline and Axilrod used a standard humidity of 65 per cent. In his review of penetration methods Starkie[13] preferred the pyramidal to the Brinell method owing to the more clearly defined impression produced.

B.S.S. 903: 1940.—This method is prescribed for determining the hardness of vulcanized rubbers. The test piece may vary from 0·3 to 1·2 cm., but comparable measurements must be made on test pieces of approximately similar thickness. These are placed on a smooth surface and the test must be carried out beyond a minimum distance from the edge. The plunger terminates in a rigid ball of 3/32 in. (2·38 mm.) diameter which is first pressed on to the rubber under a load of 30 gm. for 30 sec. An additional load of 535 gm. is then applied and maintained for 30 sec., when the position of the plunger is read again, the hardness being given by the movement of the plunger in 100ths mm. between the two readings. During the loading periods the apparatus is gently vibrated (by a buzzer to overcome friction). A temperature of 21 ± 3° C. is recommended.

All these methods have in common the property of measuring the deformation of plastic materials under concentrated loads; in some cases the surface may be broken, but this is not a criterion of measurement. However, the first three methods differ from the last in that they do not measure deformation while the major load is being applied. No doubt measurement under stress was found to be necessary for rubbers, but the same information might also prove to be of value with plastics. It is obvious that if we accept the geometrical conditions of the tests we are measuring distinct groups of properties in the two cases.

(1) The non-recoverable deformation under the conditions of test, i.e. D_{visc} + some fraction of D_{HF}

(2) Total deformation, i.e. $D_{OI} + D_{HF} + D_{visc}$

The fact that elastic deformations are involved in the Brinell test is confirmed by Starkie,[13] who found that different results were obtained if the penetration was measured during and after the application of the load. The distinction between these two procedures may be summarized as follows: in one we are measuring the resistance presented by the material to all types of deformation, and in the other we are investigating the tendency to suffer permanent visible deformation under a particular type of rough usage.

A great number of results obtained by the Brinell and Rockwell indentation tests have been recorded, and they are frequently published in the form of a wide range obtainable with a particular type of plastic. As an example, Table XXIX is taken from a monograph by Delmonte.[21] The ranges of properties shown are small enough to illustrate the rough correlation between elasticity and indentation hardness. However, the correlation is necessarily approximate and not a theoretical requisite, since the modulus of elasticity measurement is generally concerned more with the ideal elasticity, and the indentation almost entirely with non-ideal deformations. In view of the very complicated and varied deformation behaviour of plastic materials, no attempt is made in this discussion to establish a definite quantitative relation between indentation hardness and the stresses under which deformation occurs. However, for certain metals, steel in particular, an empirical relationship has been found according to which the ratio

$$\frac{\text{Ultimate tensile strength}}{\text{Brinell hardness number}} = 0{\cdot}22$$

Vivian[23] showed that the relation could be explained by taking into account the load deformation properties of the steel, the lateral and normal stresses beneath the area of contact, and the depth below the ball where appreciable plastic flow took place.

TABLE XXIX. APPROXIMATE HARDNESS AND ELASTIC MODULUS OF SOME PLASTIC MATERIALS

Plastic	Description	Modulus of elasticity (lb./in.^{2} · 10^5)	Brinell hardness
Phenol formaldehyde	Cast resin	5–15	30–45
(Moulded)	Wood flour	9–15	30–45
(Moulded)	Fabric filled	7–12	30–45
(Moulded)	Cotton	10–15	30–45
(Moulded)	Mineral filler	15–50	38–42
(Laminated)	Paper base	5–20	35–40
(Laminated)	Fabric base	5–15	30–45
Urea formaldehyde	(Moulded) α-cellulose	7–16	48–54
Polystyrene (moulded)		4–6	20–30
Polymethyl-methacrylate (moulded) ..		5–8	20–30
Polyvinyl chloride-acetate (moulded) ..		3–8	15–25
Cellulose acetate (sheets and moulded)		2–4	10–20
Cellulose nitrate (sheet)		2–4	10–20
Casein plastics		5	20

500 kg., 10 mm. ball. 2·5 mm. ball, 25 kg. load. (Data: *Modern Plastics*, 1941. Cat.)

Effect of Molecular Weight on the Indentation Hardness of some Plastic Materials

Table II shows the effect of changing molecular weight on many mechanical properties, and here it is clear that with a vinyl chloride-acetate copolymer elasticity is the property least affected. It is, therefore, not surprising to find that Carswell, Hayes and Nason[24] have found that the indentation hardness of polystyrene is not markedly dependent on molecular weight either (Fig. 61). If true viscous flow, dependent on the movement of whole molecules, is taking place under these concentrated loads, then a high molecular weight should have a definite effect in increasing the hardness number, whereas if the deformation is of the highly elastic type depending on the rotation of linkages this effect is likely to be smaller. The effect of these measurements is, therefore, to emphasize the small part played by viscous flow at ordinary temperatures.

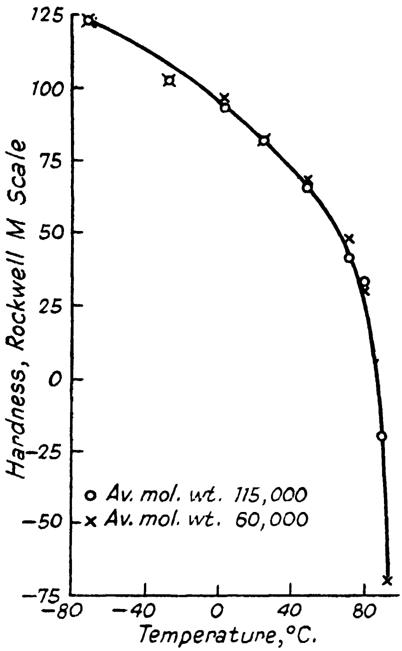


FIG. 61.—The indentation hardness of polystyrenes of different molecular weight.[24]

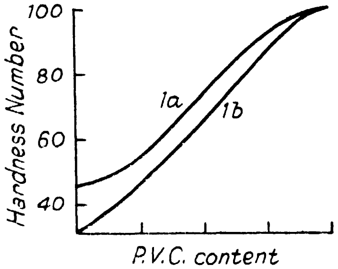


FIG. 62.—The penetration hardness of plasticized polyvinyl chloride measured immediately after the application of the load (1*a*) and after 10 sec. (1*b*).[25]

The Time Factor

The further distinction between hardness measured immediately after a load is applied and after a lapse of 10 sec. has been investigated by Saechtling[25] for polyvinyl chloride containing a number of different plasticizers. The results give two curves on which all the plasticizers are said to fall (Fig. 62), and Saechtling prefers the 10-sec. curve (1*b*) because the pointer does not move appreciably after this lapse of time. This paper does not discuss the relative permanence of the impressions produced in the different materials, but notes that the results of hardness experiments based on rebound after impact shows a minimum at a certain plasticizer concentration, i.e. it is greater for both harder and softer (more easily deformed) materials. This corresponds with the work of Church and Daynes (p. 108), who found a minimum in the recovery of rubber as the temperature rose, i.e. as the rubber became "softer." It would therefore appear that the value of rebound tests as a measure of hardness is questionable for most purposes.

The results of different indentation methods and their relation to a Shore scleroscope (rebound) test have been given by Kline and Axilrod[26] (Table XXX).

TABLE XXX. HARDNESS OF TRANSPARENT PLASTICS AS MEASURED BY VARIOUS INSTRUMENTS

Material	Sample	Thickness	Shore scleroscope number*	Vickers number†	Rockwell number‡ (15-T scale)	Brinell number§ (30 sec.)
		mil.				
Cellulose acetate ..	A1	62	57	8·7	15·1	13·0
	B1	60	58	11·0	16·2	13·1
	B2	90	61	8·4	16·0	13·9
	C1	60	53	7·0	9·9	11·5
	C3	125	54	6·2	11·2	10·9
Cellulose nitrate ..	E1	60	63	12·7	29·7	16·6
	F1	62	60	11·7	23·2	15·8
Ethyl cellulose ..	C1	60	50	6·3	7·7	10·6
Acrylate resin ..	J1	70	73	18·4	39·5	17·5
	J2	65	84	24·0	81·6	27·4
	K1	120	75	15·0	31·5	16·0
Vinyl chloride-acetate resin	L1	50	62	16·2	32·7	16·4
Vinyl acetal resin ..	M1	63	45	3·0	Too soft to measure	Too soft to measure
Styrene resin.. ..	R1	80	65	20·0	65·0	20·0
Phenol-formaldehyde resin	U1	125	80	12·6	15·5	15·8
Plate glass	X1	85	121	—	—	—
Mild steel	—	1,000	25	159‖	—	159¶

* Rebound, measured on an arbitrary scale of 140, of a hammer with a diamond striking point falling freely from a height of approximately ¾ in.; model D instrument.

† 5 kg. load applied on a diamond pyramid for 7 sec.

‡ 15 kg. load applied on a ball 1/16 in. diameter for 30 sec.; Rockwell superficial hardness tester.

§ 15 kg. load applied on a ball 1/16 in. diameter for 30 sec. (usual Brinell time).

‖ 50 kg. load.

¶ 3,000 kg. load on a ball of 10 mm. diameter.

In view of the fact that the rebound method gives a higher value of the hardness for plastics than for mild steel! Axilrod and Kline question the value of this method, but they find satisfactory agreement between the Vickers, Rockwell and Brinell tests, all of which seek to measure similar deformation properties. Separate experiments showed that with plastics both the Brinell and the Vickers tests were dependent on the duration of loading, particularly with the harder materials. A series of results obtained from the Vickers test (Table XXXI) illustrate the part played by the relatively long relaxation times in hardness tests.

TABLE XXXI. VARIATION OF VICKERS HARDNESS NUMBER WITH TIME OF LOADING[26]

Material	Sample	Vickers number		
		5 kg. load applied for 10 sec.	5 kg. load applied for 30 sec	5 kg. load applied for 90 sec.
Cellulose acetate	A1	6·3	5·8	5·9
	B1	7·2	6·7	6·7
	B2	6·8	6·3	6·3
	C1	5·6	5·2	4·8
	C3	5·2	4·6	4·2
Cellulose nitrate	E1	11·7	11·2	10·5
	F1	10·5	10·4	9·3
Ethyl cellulose	G1	5·2	4·9	4·8
Acrylate resin	J1	14·0	12·1	11·2
	J2	18·9	17·2	15·4
	K1	14·1	12·7	11·3
Vinyl chloride-acetate resin	L1	14·9	14·7	13·4
Styrene	R1	20·1	18·7	16·6
Phenol-formaldehyde	U1	13·0	11·3	9·3

A Theoretical Approach to Indentation Hardness Tests

In the case of measurements on total deformation an interesting theoretical development has arisen from the work of Scott Blair, who set out to measure the "firmness" of materials like cheese. He found that in certain cases the following relation applied between shearing stress S and strain D:

$$\psi = S\,D^{-1}\,t^{k}$$

and that in these cases, in spite of its dimensional complexity with regard to time, ψ or $\log \psi$ could be used to represent the firmness of materials previously subjected to arbitrary handling tests.[27] However, probably in most of the plastics in use to-day ψ is not independent of stress and the Nutting relation

$$\psi = S^{\beta}\,t^{k}\,D^{-}$$

must be applied.

In this relation the dimensions of ψ become complex in stress as well as time, and it cannot be satisfactorily used to represent any physical property. Nor is any measurement based on a single stress satisfactory. In order to obtain a quantity directly related to a range of times and stresses a suggestion has been made that a constant ζ representing the "intensity of firmness" should be derived from the volume of the three dimensional *S-D-t* diagram[28, 29] where

$$\text{Volume} = \frac{1}{\zeta} = \int_{S\,min}^{S\,max} \int_{t\,min}^{t\,max} D\,dS\,dt$$

On taking the arbitrary stress range of 0 to 10^6 dyne/cm.,^{2} times of 0 to 100 sec., and integrating the Nutting relation,

$$\log \zeta = \log(\beta + 1) + \log(k + 1) - \log D\max - 8$$

thus expressing $\log \zeta$ in terms of experimentally determinable quantities and giving it a meaning independent of time and stress within the specified range. However, this constant also suffers from being a dimensionally heterogeneous quantity. The analogy between the intensity of firmness and hardness, particularly in the time problem, is noted by Scott Blair, who quotes a reference by O'Neill to the difficulties associated with the time factor in measuring hardness, namely: "Is sealing wax a somewhat hard or an extremely soft material? The answer will depend on the period for which the indenting stress is maintained, and if philosophically we feel sure that sealing wax is a fairly hard material, then a limiting loading time is being specified."

This time difficulty is standardized in the customary indentation methods by specifying a particular rate of applying the stress, but this is clearly an arbitrary procedure and the type of treatment envisaged by Scott Blair appears to increase the generality of approach. However, he worked largely on very soft materials, and the particular limits of time and stress which he suggests would certainly have to be adjusted with most plastics. Furthermore, difficulty might well be met because the deformation of many plastics contains a well-defined ideal Hookean component which might have to be treated separately in the deformation equation. Such complications can, however, only be visualized at the present time; the suggestions of Scott Blair on the property called the "intensity of firmness" offer a definite possibility of further theoretical development in the measurement of the hardness of plastic materials.

REFERENCES—V

(1) O'Neill, H.: *Hardness of Metals and its Measurement* (Sherwood Press, Cleveland, 1934).

(2) Hertz, H.: *Misc. Papers*, trans. Jones and Schott, Chap. 6 (Macmillan, 1896).

(3) Hertz, H.: *Misc. Papers*, trans. Jones and Schott, Chap. 5, pp. 146, 162 (Macmillan, 1896).

(4) Fuchs, S.: *Phys. Zeit.*, **14** (1913), p. 1282.

(5) Timoshenko, S.: *Theory of Elasticity*, p. 343 (McGraw Hill, 1934).

(6) Love, A. E. H.: *Mathematical Theory of Elasticity*, 4th edition, p. 198 (Dover Publications).

(7) Auerbach, F.: *Göttinger Nachr.* (December 6, 1890); *Ann. d. Phys. u. Chem.*, **43** (1891), p. 61; *Ann. d. Phys. u. Chem.*, **58** (1896), p. 357.

For a fuller summary of Auerbach's work see Horestadt: *Jena Glass*, p. 168 (Macmillan, 1902).

(8) Raman, C. V.: *Nature*, **103** (1919), p. 113.

(9) Preston, F. W.: *J. Soc. Glass Tech.*, **10** (1926), p. 236; *Trans. Opt. Soc.*, **23** (1921-2), p. 141.

(10) Preston, F. W.: *J. Am. Ceram. Soc.*, **28** (1945), p. 145.

(11) Holland, A. J., Turner, W. E. S.: *J. Soc. Glass Tech.*, **19** (1935), p. 221.

(12) Bailey, J.: *J. Am. Ceram. Soc.*, **20** (1937), p. 42.

(13) Starkie, D.: *J. Soc. Glass Tech.*, **26** (1942), p. 130.

(14) Milligan, L. A.: *J. Am. Ceram. Soc.*, **19** (1936), p. 187.

(15) Scholes, S. R.: *J. Am. Ceram. Soc.*, **28** (1945), p. 133.

(16) Boor, L.: *Mod. Plast.* (September 1942), p. 79.

(17) *Mod. Plast.* (September 1942), p. 84.

(18) Kline, G. M., Axilrod, B. M.: *Ind. Eng. Chem.*, **28** (1936), p. 1170.

(19) Perkuhn: *Plastics*, **8** (1944), p. 316.

(20) Gehlhoff, G., Thomas, M.: *Z. Tech. Phys.*, **7** (1926), p. 105.

(21) Delmonte, J.: *Plastics in Engineering*, p. 558 (Penton Publishing Co., U.S.A., 1943).

(22) Simonds and Ellis: *Handbook of Plastics*, p. 120 (D. van Nostrand & Co.).

(23) Vivian, A. C.: *Phil. Mag.*, **35** (1944), p. 765.

(24) Carswell, T. S., Hayes, R. F., Nason, H. K.: *Ind. Eng. Chem.*, **34** (1942), p. 454.

(25) Saechtling: *Plastics*, **9** (1945), p. 375; *Kunststoffe*, **34** (1944), p. 179.

(26) KLINE, G. M., AXILROD, B. M.: *J. Res. Nat. Bur. Standards*, **19** (1937), p. 385.
(27) SCOTT BLAIR, G. W., COPPEN, F. M. V.: *J. Soc. Chem. Ind.*, **55** (1941), p. 190.
(28) SCOTT BLAIR, G. W., VEINOGLOU: *J. Sci. Instr.*, **21** (1944), p. 149.
(29) SCOTT BLAIR, G. W.: *Nature*, **152** (1943), p. 412.

CHAPTER VI

THE IMPACT STRENGTH OF PLASTICS AND GLASS

SO far we have dealt largely with the effects of static forces on various materials, and have considered the ways in which they can be deformed, and the nature of the forces required to rupture them. However, these properties are insufficient to characterize the use value of a material, and a third type of measurement is generally necessary to test the capacity to withstand sudden blows, the impact of missiles, and similar types of rough usage. In a typical impact experiment (p. 171) the energy required to break a standard test piece under specified conditions is measured. During such a test both the stress and the deformation are varying continuously and the total energy required for rupture is given by the integral

$$\int P\, d(D) \text{ for the duration of the test}$$

where P is the force and $d\,D$ the deformation taking place during the short element of time when P may be considered constant. Bailey[1] used an integral of this form to describe energy absorption under static conditions for comparison with impact measurements.

In the case of an idealized impact on a simply shaped test piece made of an ideally elastic material bending according to the theoretical relations this integration is readily made, and the energy to break may be expressed in terms of the breaking stresses, elasticity, and dimensions of the material, the dimensions usually occurring as the volume of the specimen. For instance, with a rectangular beam, the length, breadth and thickness are involved as a product in the calculated energy absorption. Sometimes there is evidence that measured impact strengths with real materials follow this relationship, though such behaviour is exceptional owing to the many other effects occurring in practice. For instance, some results exist showing a proportionality between thickness and impact strength; Gehlhoff and Thomas[2] found a linear relation between thickness and impact energy in the fracture of glass, and a similar result was found with a phenolic laminate by Koon[3] (Table XXXII); a proportionality with breadth was assumed for the latter and the effect of length was not investigated.

In this chapter impact strength is regarded as a derived property involving both the deformation and breaking properties of a material, and it is, therefore, fundamental that our approach must involve the theoretical examination of both these elements, and that impact strength will only be dominated by changes in one of them when the other is relatively constant. This point is of great importance in making comparisons between static tests and impact experiments since each of the quantities may be widely affected under conditions of impact.

TABLE XXXII. IMPACT STRENGTH OF TWO PHENOLIC-SISAL LAMINATES AS A FUNCTION OF THICKNESS WITH $\frac{1}{2}$ IN. SPECIMENS

Thickness	Impact strength of material 1	$\frac{\text{Impact strength}}{\text{Area of specimen}}$	Impact strength of material 2	$\frac{\text{Impact strength}}{\text{Area of specimen}}$
in				
1	7	14·0	5·4	10·8
$\frac{7}{8}$	6·5	14·8	4·5	10·3
$\frac{3}{4}$	4·4	11·8	4·4	11·8
$\frac{5}{8}$	4·0	12·8	3·1	9·9
$\frac{1}{2}$	4·5	18·0	2·6	10·4
$\frac{3}{8}$	2·9	15 4	2·0	10·7
$\frac{1}{4}$	2 0	16 0	1·3	10·4

The several factors which cause differences in energy absorption under impact and static conditions form one of the major problems in impact testing, but even if they were all properly appreciated—and this is not so at present—we should still lack a complete guide to material behaviour under impulsive forces. In specific conditions an almost unlimited number of other factors may influence the applicability of general principles, and of these two may be mentioned at this stage. Sometimes after a test piece is cracked considerable further energy is used up in tearing the two parts asunder, and this is included in the result given by a pendulum test of the Izod type. On the other hand, in practice the shaped article may be considered to fail when it is merely cracked, or, even if the same criteria of failure apply in each case, the differences in geometry of the test piece and the product may alter considerably the relative energy contribution of this part of the process. For a second example, two objects may be made of materials giving similar results under a wide range of impact tests, i.e. the energy required to break similar test pieces is always the same; but if the two materials have different specific gravities it would obviously be possible to discover a height from which the two objects could be dropped on to a hard surface so that one was broken and the other remained intact. This is the sort of advantage possessed by even a comparatively fragile plastic article over a heavier china one.

In these circumstances the field of impact strength remains one where qualitative rather than quantitative agreement between theory and experiment is all that can be expected; first, it would appear best to try and disentangle the many distinct factors which can operate to increase or decrease the impact strength.

If a material is broken under identical geometrical conditions by static and dynamic methods the energy absorbed in the two cases is generally different, even when the same criterion of rupture is applied to both. These differences can be experimentally investigated, and a proper understanding of them is fundamental to the investigation of the phenomena associated with impact strength. Before dealing with experimental results, therefore, some of the major effects which cause such differences are outlined in theory, largely as an expression of the author's own viewpoint, for, on the whole, little attention seems to have been devoted to the problem. However, reference may be made to the work of Bailey,[1] Morey,[4] Telfair and Nason,[5] and Hazen.[6] The latter put forward several of the factors given here and also placed considerable emphasis on energy losses in the impact testing machine. This effect is of course of greater importance from the point of view of testing technique than for the immediate question of the theory of materials.

MAJOR THEORETICAL FACTORS IN IMPACT STRENGTH

1. *The Time Factor in Fracture*

It has been shown that the static strength of plastics and glass is, in general, dependent on the rate of application of stress or on the time allowed for the material to break. Now, if we are seeking to relate the energy required to break under impact with that occurring in a static experiment we are likely to be comparing the breaking of the material in a period of 100 sec. or more with fracture in a time of the order of 10^{-3} sec. Thus the time factor involved is so large ($\sim 10^5$) that effects which seem small under different static experiments may become very important in relating static and impact experiments. The difference in energy absorption is further widened because a larger deformation is likely to occur when a larger stress is required to cause quick rupture. For example, if a solid showing ideal Hookean deformation only breaks in tension and the breaking stress at time t is given by f_t, then the greatest energy absorption in 1 c.c. of the solid is given by $\frac{1}{2} f_t^2/E$. Here, therefore, the breaking stress and its accompanying time factor occurs as the second power in the energy term. Where there is a markedly stress-dependent relaxation time, or where a linear log (rate of deformation) — stress relationship exists, a rise in the breaking stress under impact conditions may be a matter of decisive importance.

This time factor for fracture effect certainly occurs with glass, but it is to be regarded as a general element in the problem and must be considered in every theory of impact strength. It can only be neglected where experimental results show the time factor to be small over a range of time comparable to that involved in the extrapolation to impact conditions, or where there is evidence that an upper limit of breaking strength exists at all short times.

2. *Delayed Elastic Effects*

We have seen that the deformation of a plastic material may be represented by the relation

$$\text{Total deformation} = D = D_{OE} + D_{HE} + D_{visc}$$
$$= \frac{S}{E} + f(S, t) + f'(S, t)$$

Of these effects the contribution of D_{OE} is the most simple, and is, apart from limitations to be discussed later, essentially time-independent. Conclusive experiments proving the existence of viscous deformation under normal conditions with plastic materials are at present few; as far as ordinary impact strength is concerned its specific property of being permanently irrecoverable is of minor importance and any attempt which can be made at present to describe it quantitatively will be mathematically similar to that of a highly elastic deformation having a long relaxation time. For these reasons it is neglected in the following discussion, which treats in a necessarily tentative way with the possible contributions of the highly elastic deformations to impact strength.

Under D_{HE} we are therefore including all non-ideal deformations, and, as we have seen, these are often separable into a number of different components having different relaxation (orientation) times. On the relaxation time theory by itself it would appear that all deformations having a relaxation time above, say, 1 sec. can be neglected under impact conditions. However, the relaxation time is often stress-dependent, and it follows that only where this stress dependence is small or known can we predict whether the particular component of deformation will occur under impact. One or more minor delayed elastic effects capable of taking place quickly may co-exist with a larger highly elastic deformation, and they may have considerable importance in that, together with the true Hookean deformation, they give time for the larger deformations to get started.

It will be readily seen that the existence of a number of delayed elastic effects, whose stress dependence has not been investigated, offers almost insuperable obstacles to even a qualitative prediction of impact behaviour; by appealing to such factors the results of almost any impact experiment can be "explained." However, enough is known of a single large highly elastic deformation of the rubber-like variety to make certain rough generalizations possible. In Chap. IV it was shown that high elasticity was characterized by a transition temperature region where there was a marked change in the overall elastic modulus and below which the highly elastic deformations did not occur. Since the change in the amount of the deformation is a very large one in this temperature range it is reasonable to assume that it will not normally be compensated by an equivalent decline in breaking stress, and we should therefore expect many rubber-like materials to show a parallel increase in impact strength over the transition temperatures.

In other cases, especially where there is a considerable temperature range in which the extent of the highly elastic deformation occurring depends on the circumstances of stressing, e.g. this is so with plasticized cellulose derivatives, the impact strength will be mainly determined by the amount of this deformation taking place under the conditions of testing. Here the limit of extensibility provides a maximum value for the extension which can take place, but it certainly cannot be assumed that this maximum deformation will actually occur under conditions of impact. Indeed, the extent of the highly elastic deformation can be determined by the relation of the stresses required to produce a given rate of highly elastic strain, i.e. by the relation of $\left[\frac{d(D_{HE})}{dt}\right]$ to f, the fracture stress at short times.

For example, a piece of material of length l is subject to an idealized tension impact, i.e. the specimen is suddenly extended with a velocity V. We also assume that the material is one having a real stress limit f_0 (related to the original cross-section) where rupture occurs in zero time and that it shows highly elastic and ideal Hookean deformations only; the vibrational stresses are neglected.

In the impact a heavy body acts through a rigid system, and, since the specimen must extend to keep pace with the striker,

$$V = l\left[\frac{d(D_{HE})}{dt} + \frac{1}{E}\frac{dS}{dt}\right]$$

Now if $\frac{d(D_{HE})}{dt} < \frac{V}{l}$ then $\frac{dS}{dt}$ will be positive and the stress will rise until P_0 is exceeded and the material must break. Further, if we can represent the rate of deformation by a relation of the type

$$\psi(D_{HE}) \cdot \frac{d(D_{HE})}{dt} = \phi(S)$$

then there will, in general, be a unique curve relating rate of deformation with time when $S = f_0$, and this will contain the maximum rate of deformation $\left[\frac{d(D_{HE})}{dt}\right]_{f_0}^{max}$ of which the material is capable.

Hence if the test piece is struck at a velocity such that

$$\frac{V}{l} > \left[\frac{d(D_{HE})}{dt}\right]_{f_0}^{max}$$

the contribution of the highly elastic deformation is likely to be small. At lower velocities where this inequality does not apply, the stress f_0 may not, and at much lower velocities will not, be quickly reached, and the contribution of the highly elastic deformation is likely to become large and will depend on the solution of the two simultaneous equations according to which the breaking time and deformation depend on the stress to which the specimen is subjected. This may involve comparatively sudden transitions from very large to very small energy absorptions over a range of velocities of impact. These can sometimes depend on the inevitable variations in breaking stresses from one test piece to another and so give rise to big variations in results obtained with apparently similar test pieces. In the other case, where

$$\frac{V}{l} > \left[\frac{d(D_{HE})}{dt}\right]^{max}_{f_0}$$

the stress will rise steadily during the impact until rupture occurs at a value close to f_0. Under these conditions the test piece of Hookean modulus E will still extend (apart from further restrictions to be considered later) a distance of at least Lf_0/E in time Lf_0/EV, and, since the range of stresses in both is similar, the amount of highly elastic deformation will increase with the time and consequently decrease as velocity increases. This decrease should be steady and generally small.

To sum up: we see that where many types of delayed deformation co-exist almost any type of impact behaviour can be "explained," but with true high elasticity the impact strength should be temperature- and velocity-sensitive. This velocity sensitivity, which is characteristically negative (energy absorption is reduced with increasing velocity), can be sudden or gradual; uncertain results may occur in the former case due to slight changes in breaking stress from one test piece to another.

The possibility of satisfactorily investigating other effects, also operating to make impact experiments differ from static ones, is almost non-existent with materials showing large delayed elasticity, but other substances exist, notably massive glass, without this drawback.

3. *Adiabatic Effect*

When an ideal Hookean deformation occurs in a plastic material a small cooling effect accompanies it,[7] but where large non-ideal deformations occur in opposition to viscous or frictional forces emission of heat takes place and the quantity is not necessarily small. If a thin strip of plastic is subject to *slow* deformation any heat generated is easily lost and the consequences of these thermal effect are unlikely to be significant, but under impact conditions deformations must be regarded as adiabatic.

Where Hookean or small non-ideal elastic effects occur under impact the thermal changes will be small, and since the two processes operate in the opposite sense the resultant temperature changes may generally be neglected. However, this cannot be assumed for larger deformations occurring at high stresses. An attempt has been made to estimate the largest thermal effects likely to accompany the non-ideal extension[8] of plasticized cellulose acetate and cellulose nitrate. They showed a maximum tensile stress at short times and an approximate limit of extensibility.

TABLE XXXIII. THE ADIABATIC DEFORMATION OF PLASTICIZED CELLULOSE DERIVATIVES[8]

Material	Specific gravity	Specific heat	Limit of extensibility	Maximum temperature increase
				° C.
Celluloid	1·40	0·34	0·30	10
Cellulose acetate ..	1·28	0·41	0 50	4·7

From these quantities a maximum work absorption per c.c. can be calculated, assuming that the whole deformation takes place at this maximum stress, and this can be converted to a temperature rise via the specific gravity and specific heats (Table XXXIII).

In these cases the temperature sensitivity of mechanical properties is such that the temperature changes are not likely to have a large effect on impact strength in general, or to cause a difference between impact and static experiments in particular. However, this cannot be assumed for all plastics, since extensibilities of 3 (300 per cent) or more are possible, and consequently much greater temperature variations than those given here may occur. These large heat changes will take place with materials which show a large impact strength. It should also be noted that adiabatic effects are not eliminated by using geometrical arrangements, e.g. notched test pieces, giving lower total energy absorption. In such tests a large energy absorption can still occur over those restricted volumes of the material which are likely to be critical in determining total energy absorption.

To sum up: considerable thermal effects under adiabatic deformation are confined to plastics showing large highly elastic deformations at high stresses; in general they will be materials of high impact strength and the effect of the temperature changes at the beginning of the deformation is likely to increase the eventual deformation at break and further raise impact strength (assuming that the material is not reaching its limit of extensibility under normal impact conditions). These materials characteristically show marked increases in impact strength with increase of temperature.

The impact strength of glass is unaffected by this particular complication.

4. *Deviations from Theoretical Bending Relations*

Deviation in the mode of bending from that required to comply with the theoretical relations for a thin beam would lead to differences between calculated bending strength and actual maximum tensile stress in the material at the time of rupture. Similar errors occur in connection with the deformation of a beam. Such deviations from theory can derive from three causes: the material may show deformations not proportional to the stress, the beam may not be long and thin, or the bending of the test piece may be so large that the theoretical equations, which assume a small deformation only, no longer apply. Under any of these conditions the true relation between impact and static tests will be very difficult to discover. The balance between stress proportional and non-stress proportional strains in non-ideal deformation is very likely to be altered under impact so that the test piece bends in a different shape. With large Hookean deformations there will be no difference between static and impact experiments unless the stress under impact conditions is larger than under static conditions, when it is necessary to know the relation between stress and deformation for the whole test piece in order to calculate energy. This difficulty occurs with very thin glass plates whose considerable deformation under central force is neither proportional to the stress nor in accordance with simple theory.

These deviations do *not* occur in tension impact.

5. *Weight Factor*

In the case of slow impact of a weight W on a beam of weight w the assumptions can be made that at the moment of impact a common velocity of beam and striker is established and that the rest of the beam moves so that its shape remains as in a static deflection. These assumptions require that the materials shall be capable of absorbing energy at the point of contact. They lead to a factor corresponding to the loss of kinetic energy on impact which has been evaluated by Cox,[9] who showed that under these circumstances the energy of impact must be reduced by a factor

$$\frac{1}{1 + \frac{17}{35}\frac{w}{W}}$$

A similar factor has not been calculated for a plate, but it might be expected to be smaller as the fraction of the mass near the centre is less with a plate than a beam; this factor operates to *increase* the impact strength of a beam or plate as the weight of the incident missile is in effect reduced.

The weight factor is one form of energy loss during impact and other losses can occur for different reasons. These have been investigated experimentally by Tuzi and Nisida.[10] A plastic beam was struck by a heavy pendulum and the stresses estimated photo-elastically; they are then compared to those predicted from the known energy of the pendulum. The results indicate that actual stresses are only 70 to 85 per cent of those predicted, though it would appear that 2 to 3 per cent must be added to these figures as the formula used corresponds to a vertical impact and not a horizontal one as used by Tuzi and Nisida. Part of the difference is likely to be due to "damping" in the beam, i.e. the conversion of kinetic into thermal energy by the action of non-ideal deformations. In confirmation of this view it should be noted that de Bruyne[11] has reported losses of up to 24 per cent with certain plastic materials in oscillational tests. However, it should be appreciated that a major part of these energy losses are due to non-ideal deformations of the type described in Section 2.

6. *Vibrational Stresses under Impact*

An essential feature of the treatment of the ideal Hookean deformation in low velocity impact is that the test piece is conceived to be deformed in the same manner as under static conditions, so that the initial stresses when contact is first made are zero. However, as the velocity of impact is increased this assumption ceases to be even approximately true and high stresses are set up on collision which subsequently vary in a series of jumps. The precise mathematical treatment of such conditions is a matter of great difficulty, but in the simple case of the compression impact of a rigid body of mass W moving with velocity V on to a rod of mass w (Fig. 63) the sequence of events has been worked out by Boussinesq[12] and discussed more recently by Donnel.[13] A short account is given here following the treatment of Timoshenko.[14]

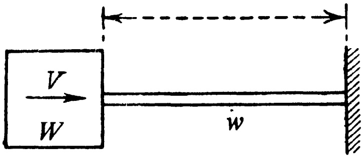
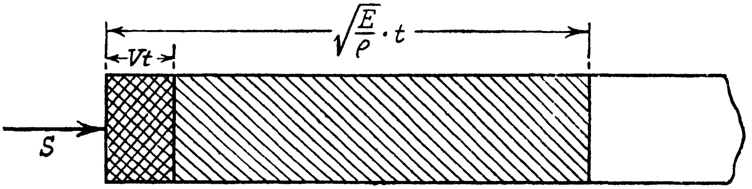


FIG. 63.—Boussinesq's theoretical impact "experiment."[12]

An illustration of the way the initial stress S_0 is brought about is given in Fig. 64, where it will be seen that $S_0 = V\sqrt{E\rho}$, where E and ρ (density) apply to the bar.* Timoshenko demonstrates that this initial compressive stress at the point of contact decreases at first according to the relation



$$\text{Stress } (S) = E \times \text{Strain} = \frac{EVt}{\sqrt{\frac{E}{\rho}}t - Vt} \sim V\sqrt{E\rho} \text{ since } \sqrt{\frac{E}{\rho}}t \gg Vt$$

FIG. 64.—Diagrammatic treatment of the vibrational stress at the point of contact.[22]

$$S_0 e^{\left(\frac{-t\sqrt{E\rho}}{W}\right)} \text{ where } S_0 = \sqrt{E}\rho$$

However, this equation only holds until the compression wave arrives back after being reflected from the fixed end of the rod, when the compressive stress is suddenly increased by an amount

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* If the same treatment is applied taking account of the properties E', ρ', of the impacting body, a similar treatment gives $S_0 = V\frac{\sqrt{E\rho E'\rho'}}{\sqrt{E\rho} + \sqrt{E'\rho'}}$. According to this treatment the initial stress is the same under tension or compression.

$2\,S_0$. By appropriate treatment the calculation can be continued in a series of steps until the stress becomes zero and contact ceases. Timoshenko gives results obtained in this way, taken from the work of Saint-Venant and Flamant,[15] as illustrated in Fig. 65. The figures are calculated in terms of a unit value for S_0 and different values of α ($\alpha = w/W$), i.e. for different impacting masses and a constant velocity of impact.

It will be clear at once that the resulting stresses do not even remotely resemble those anticipated for a steady accumulation of strain energy under slow impact. Further, it will be seen that the effect of doubling the impacting mass and changing $\alpha = 1$ to $\alpha = \frac{1}{2}$ leads to an increase of only about 10 per cent in the maximem stress though the duration for which this stress is actually applied is considerably increased. In view of the importance of the magnitude of the maximum stress in relation to the known properties of materials it is desirable to correlate the results obtained in this way with those derived from other methods of estimation. For this purpose a comparison of the results of the different calculations of the maximum stress has also been given by Timoshenko (Fig. 66). The curves given show the values of the maximum stress calculated for different values of $\alpha\,(1/\alpha)$. The upper continuous curve represents the values of $S\,(\max)$ derived from the Saint-Venant treatment, while the dotted curve represents those given by an empirical relation sometimes used, namely:

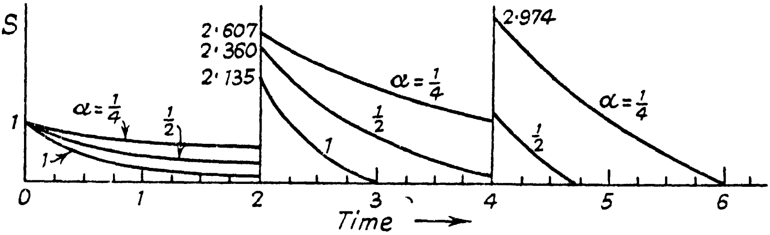

FIG. 65.—The sequence of stresses with time at the point of contact in Boussinesq's theoretical treatment of impact.[14]

$$S_{max} = S_0\left(\sqrt{\frac{W}{w}} + 1\right) = V\sqrt{E\rho}\left(\sqrt{\frac{1}{\alpha}} + 1\right)$$

The bottom continuous curve is obtained by neglecting the mass of the rod and equating the kinetic energy of the impacting object to the maximum strain energy in the rod (simple slow impact treatment). It will be seen that one major difference between the two relations can be expressed as follows:

Strain energy treatment as
$W \to 0$ Energy of impact $\to 0$ Maximum stress $\to 0$
Saint-Venant-Boussinesq relation as
$W \to 0$ Energy of impact $\to 0$ Maximum stress $\to 2V\sqrt{E\rho}$

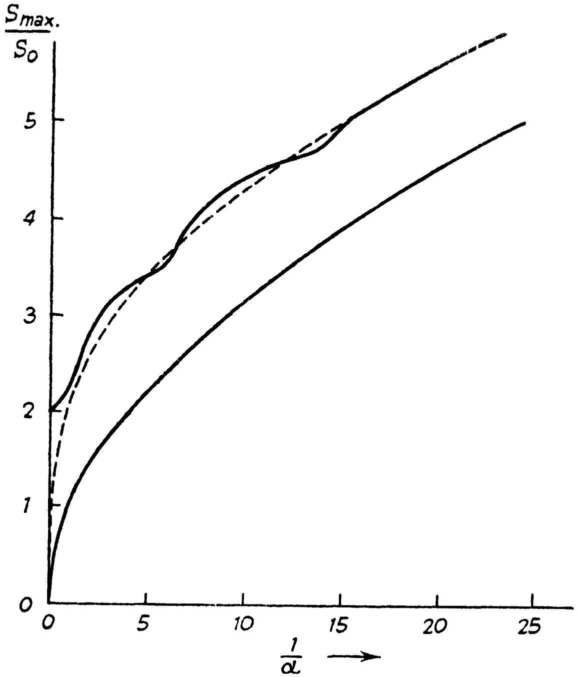

FIG. 66.—Calculated stresses for Boussinesq's impact "experiment." Upper continuous curve the exact theoretical treatment, lower continuous curve the simple strain energy treatment ($\alpha = w/W$.)[14]

These conclusions are obviously of great importance in the understanding of high veocity impact, particularly with true Hookean solids like glass. In this case we have shown that rupture with a wide range of time can be roughly expressed by the relation

$$\text{Tensile stress proportional to } (t)^{\frac{1}{12\cdot 8}}$$

or more accurately* by

$$\frac{1}{\text{Tensile stress}} - k \log t = \text{const.}$$

i.e. an increase in stress is far more destructive than an increase in the time for which the stress is applied. Further, once α becomes small, and conditions of low velocity impact are left behind, the maximum stress is proportional to V the velocity, and so it must be concluded that an increase in velocity is more likely to cause breakage than increases in the mass W (energy of impact) at a given velocity. Unfortunately it is not easy to arrange for breakage under impact to take place under the simple geometrical conditions considered by Boussinesq, but it would appear better to consider the stresses arising from high velocity impact qualitatively in terms of $V\sqrt{E\rho}$, or $2V\sqrt{E\rho}$, than in terms of strain energy and the total energy of impact. This is in general accordance with the conclusion of Boussinesq,[16] who considered, in connection with the theory of the sand blast, that if a material had a maximum extension necessary to cause rupture there would also be a maximum velocity of impact on a circular plate, given by $V = 0{\cdot}94\sqrt{E/\rho} \times$ (max. extension), above which any particle would cause permanent damage. If we replace the conception of rupture at a maximum extension by that of a maximum stress f_t so that $f_t/E =$ max. extension we get $V = 0{\cdot}94 f/\sqrt{E\rho}$, i.e. rupture occurs where $V\sqrt{E\rho} > f_t \times 0{\cdot}94$.

Further light on the significance of $V\sqrt{E\rho}$ is given if we consider unit volume of a Hookean solid breaking under a tension f_t; the maximum strain energy it can take up is given by $\frac{1}{2}f_t^2/E$; but the kinetic energy of the same volume at velocity V is given by $\frac{1}{2}V^2\rho$ and these quantities are equal when $V\sqrt{E\rho} = f_t$, i.e. this is the condition of equality of kinetic and maximum strain energy. Above this velocity (for any Hookean material for which f_t can be given a meaning) the energy required to set its mass in motion exceeds that which it can absorb in bending.

The assessment of the contribution made by these vibrational stresses to the process of fracture under impact must be carried out in relation to the geometry of the test. It is essential to recognize that the stresses are generated at the point of contact of the striker and the test piece, and that their subsequent history at this point will only follow the predictions of the Saint-Venant-Boussinesq theory when the test piece has the same shape and the material the same properties as they assumed. Naturally their assumptions are not, in general, directly applicable to most impact tests, and in practice at least two distinct cases may be considered. Firstly, in those tests where the specimen is broken close to the point of contact with the striker, for example when a weight falls on to the centre of a thin plate or a long bar, the occurrence of vibrational stresses should cause a marked reduction in the energy required to fracture the test piece at high velocities of impact, i. e. to negative velocity sensitivity. Secondly come the tests where fracture is arranged to occur at a point remote from the striker, e.g. the Izod notched bar test; and in these the contribution of the vibrational stresses cannot readily be predicted.

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* However, the implication of this formula that the tensile strength $\rightarrow \infty$ as $t \rightarrow 0$ is extremely doubtful.

The situation in those cases where elastic waves make a partial contribution to rupture has also been discussed by Morey,[17] who considers that when stress waves pass over parts of the material already under stress the stress of the pulse is momentarily added to the existing stress and may carry it over the limit for fracture. Morey also suggests that the intensity of these waves becomes reduced when they are propagated in a material containing heterogeneous elastic constants with a wide range of relaxation times. It would appear that such materials must contain a range of short relaxation times if the elasticity is to operate under impact conditions and that the overall elasticity measured by vibration techniques should depend on the frequency.

The damaging effect of elastic waves will always be reduced if they are propagated in materials with a high damping capacity, i.e. in which potential and kinetic energy are not readily interchangeable.

7. *Other Effects in Impact*

The six factors outlined by no means exhaust the numerous possibilities which have to be considered in the comparison of dynamic and static testing, and, apart from the likelihood that undefined factors still exist, there remain many others. Among them are the energy losses in the testing machine and the errors involved in the method of gripping the test piece. For instance, where the holder has a sharp edge, or where excessive pressure is applied across the grain of a laminated material, the results may be appreciably affected. Another effect of great importance is the notable reduction in impact strength brought about by the existence of notches, i.e. points of stress concentration in the material. As the effect of these is considerable, as they are often peculiar to certain materials, and as irregularities of shape often occur in use, the impact testing of notched samples is often preferred or specified. In these and other tests the material may be broken into separate pieces by the striker, as in the ordinary Izod test, causing additional energy contributions which are included in the result obtained. Among them is the kinetic and rotational energy of the broken fragments, and any additional energy, often considerable with complex laminated materials, which is used in tearing the specimen apart after the first crack is formed. Where the latter is large there will be a marked difference between the energy to fracture the specimen and the energy absorbed in breaking it up; with a material like laminated glass the energy required to crack the glass may be only about 20 per cent or less of that necessary to break up the material into separate pieces.

Impact Strength of Glass

The problem of impact strength and its relation to slow deformation is greatly simplified with materials showing mainly the ideal Hookean type of deformation. In such, according to the classification given above, we should expect only the time factor, vibrational stresses, possibly the weight factor and certain energy losses during impact to operate—provided always that samples are chosen where static bending occurs according to the theoretical relations. Massive glass is outstanding in that all deformations other than the Hookean deformation are certainly small and, therefore, its behaviour under impact is worthy of special theoretical consideration.

Of the three factors mentioned previously as applying to glass, it is to be noted that two of them, the weight factor and vibrational stresses, are minimized by using impact conditions in which a heavy weight strikes the glass at a low velocity. There remains the time factor in fracture. In these circumstances the breaking stresses calculated from the energy of impact and the theoretical bending relations should be noticeably larger than those occurring under forces slowly applied, and the increase should correspond, at least roughly, with that predicted for the known time variations in the bending strength of glass.

In Chap. III it was shown that the bending strength of a single piece of glass is a measurement at present without much physical significance, and that only averages of a number of strength measurements, together with such statistical parameters as the standard deviation or the coefficient of variation, were of value. This applies with all the more force to impact measurements, where the Hookean energy term will be of the form

$$\tfrac{1}{2}f_{B,t}^2/E$$

where $f_{B,t}$ is the bending strength in time t. If we write $f_{B,t}$ in individual cases as

$$f_{B,t}\left(1 \pm \frac{\mathrm{v}}{100}\right)$$

it follows that impact strength will contain terms approximately of the form

$$(\tfrac{1}{2}f_{B,t}^2/E)\left(1 \pm \frac{2\mathrm{v}}{100}\right)$$

i.e. the apparent coefficient of variation will be roughly doubled; since 20 per cent is a common value of this coefficient for the bending strength impact variations of 40 per cent are to be expected. Thus, the errors in impact experiments from this source are liable to be particularly high and averages of less than 25 tests are not likely to be accurate. This wide variation in impact tests was found in the experiments of Gehlhoff and Thomas[2] and other workers.

In low velocity impact experiments with a material like glass having a high modulus of elasticity it is also generally possible to neglect the distance through which the glass bends during impact in comparison with the fall of the ball or hammer, i.e. the energy of impact can be taken as simply the mass of the striker multiplied by the distance fallen at the point of contact with the glass. This energy is then related to the bending and breaking energy of the beam or plate via the appropriate linear equations for bending and rupture using the relaxation

$$\text{Strain energy} = \int P\,d(D) = \tfrac{1}{2}\text{ central force } \times \text{ deformation.}$$

In the case of a beam supported at its opposite ends the deformation and rupture relations are

$$\text{Deformation} = \frac{\text{central force} \times l^3}{4\,E\,b\,h^3} \text{ and}$$

$$f_{B,t} = \frac{3 \times \text{central force} \times l}{2\,b\,h^2}$$

giving under impact conditions[17]

$$f_{B,t} = \sqrt{\frac{18\,E \times (\text{Energy to fracture})}{l\,b\,h}}$$

where b is the width, l the length and h the thickness. For a square plate simply supported[18]

$$\text{Deformation} = \frac{0\cdot 1265\,a^2\,(\text{central force})}{E\,h^3} =$$

$$f_{B,t} = \frac{\text{central force}}{h^2}\,(1 + \sigma)\left(0\cdot 485 \log \frac{2a}{\pi h} + 0\cdot 52\right)$$

where a is the side of the square plate.

The comparison of derived breaking stresses f_B under bending and impact is most easily carried out for glass beams, and such experiments have been recorded by Williams,[19] Schmeer,[20] Preston[21] and Haward.[22] In all these, higher values were obtained under impact than static bending, but in the experiments of Williams, who used a relatively light striker and large pieces of glass, ratios of only 1·0 to 1·2 in the two stresses are to be derived; though Preston and Schmeer obtained ratios averaging about 1·4. In the later experiments carried out by Haward care was taken to use a heavy (1·1 to 1·6 kg.) pendulum, with relatively light (0·039 to 0·079 kg.) glass beams, and the results were analysed to give the ratio of fast (impact) and slow bending strengths. These ratios were then compared with those predicted by the empirical relation of Holland and Turner,[23] according to which:

$$\frac{f\,\text{fast}}{f\,\text{slow}} \propto \left(\frac{t\,\text{slow}}{t\,\text{fast}}\right)^{\frac{1}{12\cdot 8}}$$

The results are shown in Table XXXIV. The agreement between the last two columns indicates that the impact strength in these experiments was largely determined by the higher stresses required for the fast fracture.

TABLE XXXIV. FAST AND SLOW BREAKING OF GLASS BEAMS

h	f, slow	t, slow	f, fast	Impact velocity	Fast deformation	t, fast	$\frac{t\text{, slow}}{t\text{, fast}}$	$\frac{f\text{, fast}}{f\text{, slow}}$	$\left(\frac{t\text{, slow}}{t\text{, fast}}\right)^{\frac{1}{12\cdot8}}$
cm	kg/cm^2	sec	kg./cm^2	cm/sec	cm	sec			
0·205	950	9·5	1,380	85	1·6	0·038	250	1·45	1·54
0·205	660	6·6	850	85	1·0	0·023	290	1·29	1·56
0·284	800	12·5	1,240	105	1·03	0·020	625	1·55	1·65
0·284	720	14·0	1,110	105	0·92	0·017	820	1·54	1·69
0·284	650	15·5	1,050	105	0·87	0·017	916	1·62	1·70
0·415	681	29	1,220	105	0·70	0·013	2,230	1·80	1·87
0·415	718	28	1,150	105	0·66	0·0125	2,240	1·60	1·87
0·415	590	24	1,010	105	0·57	0·0110	2,206	1·72	1·84
0·415	572	23·5	970	105	0·55	0·0105	2,240	1·70	1·87

TABLE XXXV. FAST AND SLOW BREAKAGE OF GLASS PLATES

Size of frame and thickness	Slow breaking force at centre $= P_s$	Impact energy	Calculated central breaking force (fast) P_f	Impact velocity	Fast deformation	$\frac{t\text{, slow}}{t\text{, fast}}$	$\frac{P^f}{P^s}$	$\left(\frac{t\text{, slow}}{t\text{, fast}}\right)^{\frac{1}{12\cdot8}}$
cm	kg	kg cm	kg	cm sec	cm			
$13\cdot5^2 \times 0\cdot21$	26·9	5·6	56	106	0·20	8,100	2·1	2·0
$29^2 \times 0\cdot21$	26·9	10·9	46	155	0·27	4,900	1·7	1·9
$13\cdot5^2 \times 0\cdot28$	49	6·5	90	113	0·144	14,300	1·8	2·1
$29^2 \times 0\cdot28$	49	13·7	65	164	0·42	5,900	1·3	2·0
$13\cdot5^2 \times 0\cdot41$	81	14·0	247	166	0·114	21,000	3·0	2·2
$29^2 \times 0\cdot41$	81	14·0	110	166	0·25	10,000	1·4	2·1
$29^2 \times 0\cdot41$	77	20·5	140	213	0·30	19,000	1·8	2·1

The procedure in Table XXXIV was then repeated for the slow central impact of a 0·88 kg. steel ball-bearing on simply supported square panes of sheet glass (Table XXXV).

Tables XXXIV and XXXV show that the agreement between the predictions of the fracture time relation and the results of impact experiments is satisfactory, taking into account the inevitable errors involved, but that this agreement is closer with beams than with squares. One reason is that the coefficient of variation obtained in the breaking of beams under impact is smaller than with squares, the figures being 20 to 30 per cent and 35 to 55 per cent respectively. This difference corresponds to a parallel difference in "v" obtained with the two different modes of rupture in static experiments. Thus the experiments with beams yield the more reliable average value for the energy required to cause fracture. It is possible to assemble the pieces of the squares after fracture, and so to compare the cracking patterns obtained under slow impact with those given under static conditions. The general similarity in the form of cracking (Plate III) furnishes further evidence of an analogy between the two processes; according to this view the sequence of events in each is therefore as follows. The glass is gradually deformed by the applied load until the maximum tension beneath the point of loading exceeds the breaking stress under the conditions of the experiment, during this period potential energy is stored in the glass. However, once fracture takes place this potential energy is released by the spreading cracks and operates to build up stresses at the crack tips, and so the process by which the cracks extend is one of explosive violence. A spark photograph which illustrates this development, and shows the presence of highly stressed regions at the tips of cracks spreading in a plate of glass, has been published by Edgerton and Barstow[24] (Plate VIII (*b*)). All these results are construed as being in agreement with the view that the time factor plays a major part in causing the energy required to break glass under slow impact to be larger than is necessary under statically applied forces.

However, it is to be noted that the time factor operates in the same sense as the energy dissipation factor, i.e. to increase strength under impact conditions. If the energy losses were as large as those obtained by Tuzi and Nisida with a plastic beam[10] it would follow that another factor is operating to reduce the impact strength of glass even under these conditions. However, it does not seem possible to reduce the contribution of the time factor substantially since Preston has shown the bending strength time curve to be continuous down to 10^{-2} sec. and his values fall within 15 per cent of those predicted by the Holland and Turner relation. Obviously there is room for energy losses of about 10 per cent within the accuracy of the work, but a reduction of 20 per cent in the f(fast)/f(slow) ratio for beams, which is what the work of Tuzi and Nisida would suggest, would bring the time factor below accepted values. The best assumption seems that the energy losses in a Hookean solid like glass are much less than in the plastics used by Tuzi and Nisida, a conclusion in accordance with known properties.

Further support for the time factor hypothesis comes from the consideration of the properties of toughened glass, where the static and impact strengths of a sample have been determined by the same author,[25] and treated by a method based on the principles already outlined. The toughened glass is first compared with a piece of sheet glass broken under similar conditions so that the bending strength can be divided into the two components

$$f_B \text{ (toughened glass)} = f_B \text{ (sheet glass)} + K \text{ (toughening factor).}$$

In slow rupture the quantities are, respectively,

$$1{,}970 \text{ kg./cm.}^2 = 960 \text{ kg./cm.}^2 + 1{,}010 \text{ kg./cm.}^2$$

It follows that any increase in slow impact energy over slow breaking energy with this glass must be due to the alteration in the 960 kg./cm.^{2} term under conditions of impact. This alteration can be calculated either by the Holland and Turner relation or by analogy with pieces of sheet glass whose impact strength was also determined. The results obtained are given in Table XXXVI.

TABLE XXXVI. THEORETICAL AND EXPERIMENTAL RESULTS FOR THE ENERGY REQUIRED TO FRACTURE A PIECE OF TOUGHENED GLASS UNDER IMPACT

Slow energy for fracture (measured)	Impact energy calculated from Holland and Turner relation[23]	Calculated by analogy with sheet glass	Experiments with 0.88 kg ball
37 kg /cm.	87 kg /cm	73 kg./cm.	79 kg /cm.

Here again the results support the theory that the time factor is the dominant one for Hookean solids at slow velocities of impact.

At first sight this theory suggests that if the impact strength of different types of glass is measured at low velocities it should decrease as the modulus of elasticity increases, and increase with increases in the bending strength. This conclusion is not supported by the results of Gehlhoff and Thomas[2] on the effect of changing composition on impact strength, but it cannot be said either that they supply definite contrary evidence since, firstly, the time factor is not likely to be independent of composition and was not determined for their glasses, which differ markedly from most soda-lime-silica glasses upon which the measurements of Holland and Turner, and Preston were carried out, and secondly, whereas bending and tensile tests are performed on circular or elliptical rods impact experiments are made with small rectangular beams. Nevertheless, their figures do serve to illustrate, except in the case of B_2O_3, that the addition of the various basic oxides to the soda-silica base glass does not have a very marked effect on impact strength (most of their figures fall in the range $2 \pm 0{\cdot}3$), i.e. impact strength is not very sensitive to the composition of the glass.

Effect of Increasing the Velocity of Impact

By using a series of ball bearings of different sizes it is possible to investigate the average energy and height of fall required to break simply supported glass panes of any particular size. Such investigations with sheet and toughened glass squares of sides 4 to 12 in. have been carried out by Haward[22] and with 2 in. circles by Bailey,[26] and the results obtained are in general agreement. As the velocity of impact is increased (size of ball decreased) there is a very marked fall in the energy required to crack the glass (Fig. 67). This fall in energy is accompanied by changes in the cracking pattern, as may be seen by comparing Plates III and IV. It has been shown[27] with toughened glass that this falling off in energy to break also occurs in a similar way if a loaded striker is used to give a constant curvature in contact with the glass (Fig. 68). This falling-off effect cannot be accounted for by the operation of the "weight factor" since this would act in the opposite sense and so tend to increase the energy to break with light balls. It appears, therefore, that glass is subject to a severe form of velocity sensitivity despite only ideal Hookean deformations being involved; to explain this vibrational stresses must be considered. If we take $V\sqrt{E\rho}$ as a rough indication of the initial stress waves in the glass we find that with $\rho = 2\cdot5$ and $E = 700{,}000$ kg./cm.,^{2} and neglecting the elasticity of the steel ball in comparison with the glass the following results are obtained:

$V = 400$ cm./sec. (9 m.p.h.) (Sheet glass)	$V\sqrt{E\rho} = 530$ kg./cm.^{2} (Sheet glass)
$= 900$ cm./sec. (20 m.p.h.) (Toughened glass)	$= 1{,}200$ kg./cm.^{2} (Toughened glass)

i.e. the falling off of energy to fracture does occur at those velocities

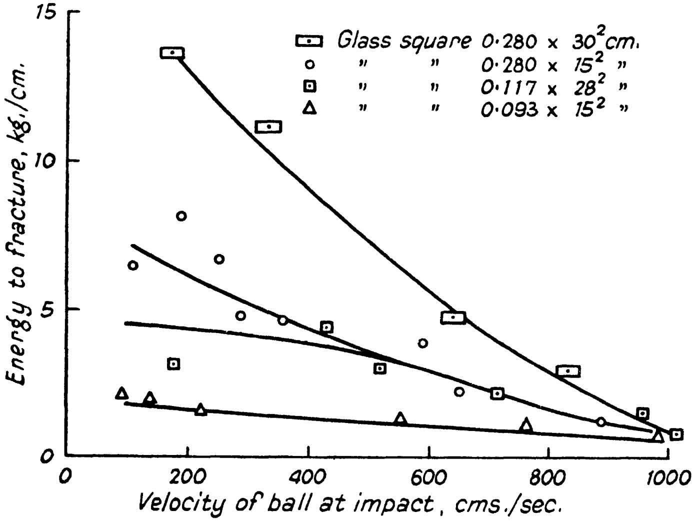


FIG. 67.—The relation between the energy to fracture and the velocity of impact for glass squares of different sizes.[22]

where $V\sqrt{E\rho}$ is becoming comparable with the bending strength of glass and toughened glass. These results may therefore be considered to agree with the view that what we have called vibrational stresses, arising from the collision of two elastic materials, play a major part in cracking the glass at high velocities.

At first this conclusion seems to contradict the work of Edgerton and Barstow,[28, 24] who showed that when glass was broken by a striker arrangement at velocities in the 400 to 1,000 cm./sec. range rupture a short time after impact was caused by tangential bending stresses after some deformation had taken place. Also, in other experiments they found that no connection could be observed between the movements of the wave fronts and the propagation or initiation of cracks. The conception of vibrational stresses must be interpreted in accordance with these results; but at present there seems no reason to discard the theory that in fast impact on the centre of a simply supported glass square both the normal pressure on the glass, and the tangential tensions below the striker which cause fracture, can be brought discontinuously up to the breaking value when $V\sqrt{E\rho}$ is comparable to the breaking stresses; nor that the developing stresses differ from those under slow deformation in a manner similar to the difference between the results of the treatment of Boussinesq for a compressed rod and those given by ordinary static compression. In such instances the breaking stresses are reached at smaller deformations and therefore with smaller energy absorptions than with slow fracture as the bending stresses immediately round the point of contact between striker and glass are increased by the necessity of communicating kinetic as well as potential energy to remote parts of the pane. In high velocity fractures the type of support might be expected to play a decreasing part in deciding the energy required to crack the glass, since the essence of this theory is that high stresses are generated at the time of initial contact before the

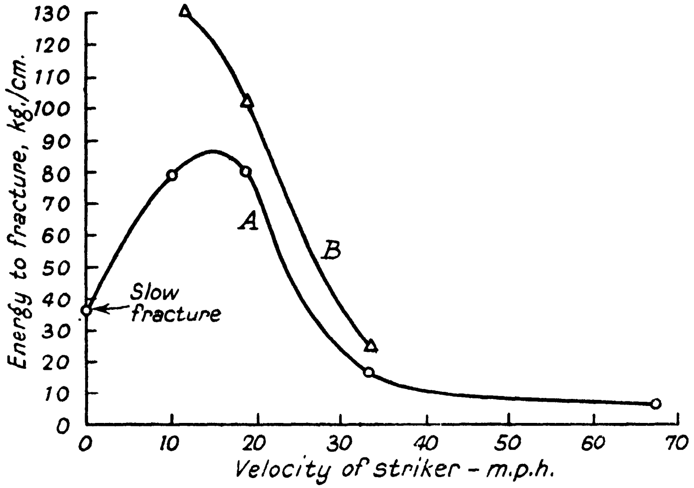


FIG. 68.—The energy required to fracture 12 in. × 12 in. × $\frac{3}{16}$ in. toughened glass squares under impact at different velocities. Curve *B* is based on experiments with a different sample of glass. In this case a loaded striker was used so that the curvature of the surface in contact with the glass was constant in the three groups of experiments.[27]

glass has started to bend appreciably. Bailey[26] has confirmed this. He found: (*a*) that at low velocities the energy to crack was less on an iron than on a wooden support, but that this divergence disappeared at higher velocities. His experiments made with 2 in. diameter circles seem to have been somewhat more sensitive to the type of support than those of Haward with larger squares; he also found (*b*) that if the glass is hung on cloth in a vertical plane it can still be broken under impact at suitable velocities, and that under these conditions also the energy to break falls to very low values with small balls and high velocities.

By setting up an arrangement whereby a ball was caused to rise vertically with a known velocity and strike the centre of the bottom surface of a steel or glass plate, Bailey investigated the communication of energy through the plate to a ball on its upper surface (Plate IX (*c*)). The height to which the rebound ball rose was indicated by the trace on the smoked glass plate. Two such traces are shown in Plate IX (*a*) and (*b*) for a steel- and an ivory-impacting ball respectively. It will be seen that the steel ball with the higher velocity and elasticity modulus gives a much more concentrated effect, and the ivory ball gives impulses widely distributed right to the edge of the plate. The concentration of stresses at the edge is of interest, and in accordance with Bailey's observation that small pieces of glass frequently break from the edge instead of the point of impact. This effect is relatively less common with larger specimens, though it can also occur.

In all these examples it has been assumed that the size of the circular missile was of small importance. This assumption may be justified when the glass breaks in tension from the lower surface, particularly where deformations and the bending stresses can be derived from the theory of deformation of the plate under a concentrated central force, but with small balls travelling at high velocity and thick plates of glass it is quite possible for the glass to break first under the Hertzian forces round the circle of contact. Plate X (*a*), (*b*) and (*c*) shows an example from the work of Edgerton and Barstow[27] where both methods of rupture are taking place simultaneously under impact, and Plate X (*d*) gives an example of a perfect cone knocked out of $\frac{1}{2}$ in. glass by a $\frac{1}{2}$ in. diameter steel ball bearing falling 26 ft. Under impact a number of varying stages between the ring crack and the full "cone" effect can be obtained, but under static experiments only the initial circle and small extensions into the glass have been reported.

There is an essential difference between the experiments of Edgerton and Barstow, and Haward. In the beam shown in Plate X(*a*) the Hertzian cone is formed at the point of contact but does not extend until after the glass has broken under bending tension at the opposite edge, whereas Haward knocked an undamaged "cone" out of the glass by continuous extension of the original Hertzian ring crack. This difference is to be ascribed to differing geometrical conditions and velocities of impact. It should be noted that when breakage takes place under the Hertzian forces at high velocity it can occur almost immediately under the influence of those contact stresses from which the stress wave originates, and without appreciable bending of the test piece as a whole.

We may now sum up the effects occurring in the breakage of glass under impact:

(1) Under slow impact the energy to fracture is greater than when similar pieces are broken statically. The increase is in rough agreement with that which would be predicted from the known time factor for the fracture of glass in tension.

(2) At velocities of impact above 200 cm./sec. ($\sim$ 7 ft./sec.) with steel balls and 4 in. to 12 in. glass squares a decline in energy to fracture sets in which can be explained as being due to vibrational stresses.

(3) With small areas of contact, high velocities, and thick pieces of glass, fracture occurs at the point of impact on the upper surface under the influence of Hertzian forces.

Methods of Testing Plastic Materials

The greater part of the current impact testing of plastic materials is carried out by the Izod and Charpy notched bar tests. However, many other methods of testing have been applied, and of these perhaps the most important are those where the energy required to crack the test piece is measured. One specification[29] where this type of test has been applied requires that acrylate sheets supported on three ¼ in. metal rods situated at the corners of an isosceles triangle shall withstand specified impacts from a falling steel ball without splintering or cracking.

In the Izod and Charpy tests a bar, commonly ½ × ½ × 2½ in. for the Izod and ½ × ½ × 5 in. for the Charpy tests, is broken by the swing of a heavy pendulum. The energy taken up by the impact is measured by the difference in the height to which the pendulum actually rises compared with that to which it would have risen if no test piece had been there. An Izod testing machine is shown in Plate XI (*a*); the marker on the dial is carried round by the movement of the striker and remains on the left-hand scale to indicate the Izod impact strength of the material. In this Izod-type machine the test piece is in the form of a small cantilever, but with the Charpy impact test it is in the form of a beam to be broken at the centre. Illustrations of suitable test pieces as recommended by the British Electrical and Allied Industries Research Association have been published[30] and one of these, for the Izod machine, has been incorporated in B.S. 903: 1940 (Fig. 69). Somewhat similar test pieces have been described in current American specifications, but here the angle of the notch is reported to be $22\frac{1}{2}$°, its depth 0·100 in. and thickness at the bottom 0·01 in.[31] These differences will naturally mean that results are not precisely comparable with the differing test pieces. On the question of notched and unnotched impact testing the article[30] recommends that unnotched specimens should be used when a uniform structural element with supported boundaries is likely to be subject to a rapidly applied bending stress, but that notched test pieces should be used where there are structural features tending to localize the stress.

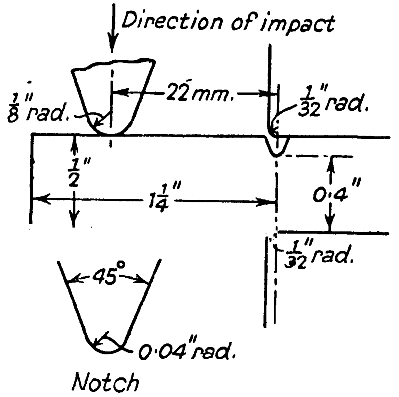


FIG. 69.—A diagram of an Izod test piece.[30]

A series of results obtained by a Charpy notched impact test and by ball drop tests on $6\frac{1}{2}$ in. diameter plastic discs gripped between rubber gaskets, has been presented by Axilrod and Kline[32] in connection with their survey of materials suitable for use in aircraft (Table XXXVII). It will be seen that there is a general parallelism between the results given by the two methods; the figures also illustrate the typical superiority of the cellulose materials under impact compared with other thermoplastics. The notable reduction in the notched impact strength with decreasing temperature is a common property with many plastic materials,

TABLE XXXVII. CHARPY AND DROPPED BALL IMPACT TESTS ON TRANSPARENT PLASTICS

Material	Sample	Thickness	Charpy impact strength (notched) ft.-lb /in. of notch		Ball height	Ball impact strength Average No falls required for failure
			70° F.	25° F.		
		mil.			ft.	
Cellulose acetate ..	A1	65	2·8	0·51	65	2·5
	A2	96	3·2	0·37	50	7
	A3	135	2·1	0·25	50	9
	B2	94	1·9	0·33	65	6
	B4	98	3·0	1·51	65	2·5
	B5	100	3·6	1·53	65	10
	B6	67	2·7	0·89	65	1
	B7	95	2·4	1·16	65	6
	B9	92	2·3	0·29	65	5
	C1	57	2·8	1·02	65	3
	C3	125	2·4	0·84	65	9
	D1	165	2·3	0·30	50	6
Cellulose nitrate ..	E1	66	3·8	2·13	65	4
	F1	63	4·4	2·60	65	4·5
Ethyl cellulose ..	G1	59	3·1	2·49	—	—
Acrylate resin ..	K1	117	0·46	0·33	3	2
	K4	88	0·45	0·26	—	—
	K7	222	0·44	0·37	10	2
	K8	218	0·40	0·36	10	3
Vinyl-chloride-acetate resin	L3	102	0·4	0·15	8	2
Vinyl acetal resin ..	N1	122	2·9	0·65	65	11·5

Application of the Theories of Impact Strength to Plastic Materials

From the theoretical discussion it is clear that the impact strength of plastic materials is so complex a subject that exact prediction of results is largely impossible. It is, in fact, easy to predict almost any result by appealing to one or other of the perfectly possible effects. All that can be expected is to establish certain probable correlations and the particular circumstances under which they are obeyed.

If we divide the energy taken up by the most highly stressed part of a plastic test piece where rupture is presumed to occur under tension into its ideal Hookean and non-ideal elastic portions (and a similar relation could be set up for rupture under shear) we get

$$\text{Energy taken up} = \tfrac{1}{2} f_t^2/E + \int_{S=0}^{S=f_t} S\, d(D_{HE})$$

where f_t is the tensile fracture stress of the material under the conditions of the test.

It should be noted that this relation does not include any energy taken up in the tearing process after fracture; to obtain any conclusions out of it we can divide our plastic materials into two sorts.

(1) Those where the Hookean deformations predominate—typically the thermosetting resins but also thermoplastics (polystyrene) at temperatures well below their elastic temperatures.

(2) Those where the highly elastic type of deformation occurs and greatly exceeds the Hookean deformation—typically the thermoplastic materials above their thermo-elastic transition point.

In making these distinctions we are making simplifications which cannot universally apply, since all plastic materials show something of each type of deformation and it is always possible to have arrangements in which a small additional deformation at a particular point may make it possible for the test piece as a whole to take up very much more energy. For this reason, predictions are most likely to be obeyed in the simplest geometrical conditions.

Nevertheless, we can see that in the first sort, as with glass, we are largely dealing with changes in $\frac{1}{2}f_t^2/E$ and concerning this quantity two conclusions appear possible. Firstly, it appears well established that f_t increases as $t \rightarrow 0$ with most plastics, and we should expect the energy taken up under impact to be more than in slow bending under similar conditions. At present experimental evidence on this point is meagre, but some unpublished experiments by the author have shown that polystyrene squares take up considerably more energy under slow impact than with static bending, and the work of Telfair and Nason[33] has shown that in an unnotched Charpy test a wood flour-filled phenolic resin takes up more energy than in slow bending, the difference according with the observed time factor for fracture. Secondly, it is clear that both the quantities f_t (or f_s) and E, in general, decrease steadily as the temperature is raised, so the impact strength under these conditions may increase or decrease steadily (or both) over a temperature range, but sudden transitions are unlikely so long as D_{HE} is largely absent.

This generalization seems to be well supported by the experimental results for thermosetting and hard thermoplastic materials. Carswell, Hayes and Nason[34] showed that the Izod unnotched impact strength of polystyrene decreased slightly with increasing temperature over a considerable temperature range (Fig. 70), and other examples of an almost constant impact strength over a wide temperature range have been presented.[35] These experiments were made with a falling ball test on a thermosetting resin and on cast methacrylate; a ½ lb. ball was dropped from increasing heights on to a $\frac{3}{16} \times 15 \times 20$ in. specimen until fracture occurred (Table XXXVIII).

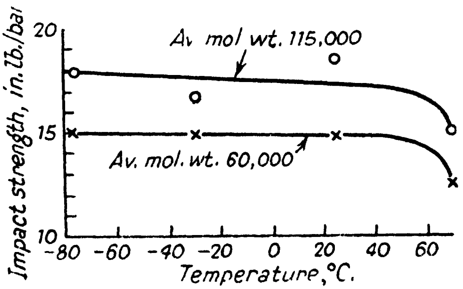


Fig. 70 —The impact strength of polystyrene as a function of temperature.[34]

With methacrylate resin Burns and Werring[36] also found that temperature had no decisive effect. Over the range 75 to 120° F. they found that the Izod test gave an increase in the impact strength with increasing temperature when notched samples were used, but with unnotched samples the opposite occurred. Thus, the existence of plastics whose impact strength is nearly independent of temperature over a wide range may be regarded as well established.

Table XXXVIII. Height to Fracture Rectangular Resin Sheets with ½ lb. Ball

Temperature, F	Height, ft	
	Cast methacrylate	Thermosetting resin
70	18	42
- 40	21	42
0	21	45
32	18	36
70	18	33
120	12	18

Another important feature of the results of Carswell, Hayes and Nason[34] is their evidence showing the effect of molecular weight in increasing the impact strength of polystyrene. In this respect their results are similar to those for polyvinyl chloride-acetate[37] (Table II), which show that when the molecular weight is raised both tensile and impact strength increase, but the elastic modulus is not greatly affected. Gloor's experiments[38] also show a marked increase in the impact strength as the (viscosity) molecular weight increases. He found that plasticized ethyl cellulose and cellulose acetates both gave marked increases in impact strength measured at − 40° F. as the intrinsic viscosity was increased in the region 1·0 to 2·5; it is probable that these plastics show a mainly Hookean deformation at such low temperatures. Wherever this is so the impact strength should be controlled by the quantity $\frac{1}{2}f^2/E$ and the increase in impact strength with molecular weight will follow directly from the known increase in f, provided that any changes in E remain small; but there is not much experimental evidence showing the effect of molecular weight on Hookean elasticity, though the assumption that the changes involved are not large seems reasonable theoretically.

Another consequence of impact strength being controlled by the quantity $\frac{1}{2}f^2/E$ is that where the fracture strength is affected by any given treatment, without the elastic properties of the material being altered, the impact strength should always change in the same sense as the static strength; in this connection Bartoe[39] has measured the flexural strength and the unnotched Charpy impact strength of Plexiglas (acrylic) resin for different types of surface treatment. If the material is showing largely Hookean elasticity we should expect the following relation to hold:

$$\frac{(\text{Flexural Strength})^2}{\text{Charpy, unnotched impact strength}} \sim \text{constant}$$

Bartoe's results are given in Table XXXIX. It will be seen that the theory is, on the whole, supported by the experimental results.

Impact Strength in Relation to the Highly Elastic Deformation

It is not necessary that a highly elastic deformation, measurable under conditions of slow deformation, should also be capable of occurring quickly and therefore of contributing to impact strength. Where high elasticity does not contribute to impact strength the drop in fracture strength where the polymer softens near its transition point will cause a sharp drop in impact strength, i.e. as the temperature is raised a point is reached where the impact strength suddenly falls. Examples of this type of behaviour are given by polystyrene (Fig. 70) and methacrylate (Table XXXVIII). Some evidence that D_{HE} does not in fact occur readily at high rates of deformation with plasticized polymethyl methacrylate is presented later. A drop in impact strength at high temperatures is also characteristic of the thermosetting resins which do not show true high elasticity.

On the other hand, with the cellulose esters and ethers, polyvinyl butyral and some other plastics, it is a characteristic and valuable feature that the highly elastic deformation does occur under impact conditions. Naturally, wherever this is so impact behaviour will be dominated by the properties of D_{HE} since it greatly exceeds the Hookean deformation in magnitude. Thus, these plastics show a typically high impact strength which increases rather suddenly in the temperature range where high elasticity begins to operate. The characteristic properties of such materials are illustrated in Fig. 71, taken from the work of Carswell, Telfair and Haslanger.[40] The results clearly show the favourable effect of increasing the temperature with plastics of the cellulose and acetal type; a similar effect can often be obtained by the addition of a suitable plasticizer. In Chap. II an analogy was drawn between the results obtained by the addition of a plasticizer and the effect of raising the temperature. It is therefore in accordance with this view that the addition of plasticizer should normally raise the impact strength of cellulose plastics.[41] However, exceptions to this rule exist, and one of them is included in Table XIV, where the addition of a solid toluene sulphonamide plasticizer decreases the

TABLE XXXIX. THE BENDING AND IMPACT STRENGTH OF ACRYLATE BEAMS[8]

Surface treatment	Impact strength ft./lb.(a)	Flexural strength lb./in.^{2}(b)	$\frac{b^2}{10^6(a)}$
Polished to remove scratches	3·2	13,750	59
Belt sander at 45°	3·0	12,800	54
Belt sander perpendicular to length ..	1·6	9,530	57
Belt sander perpendicular to length but coated with plexiglass solution ..	2·2	13,000	76
Belt sander parallel to length	3·5	13,500	52
Tension side sander perpendicular and compression side parallel	1·6	9,300	54
Scratched 0·100 in. deep	0·35	5,350	84
Scratched 0·050 in. deep	0·45	5,550	68
Scratched 0·025 in. deep	0·67	6,050	56
Scratched 0·020 in. deep	0·74	6,100	50
Scratched 0·009 in. deep	1·94	13,200	90

impact strength of a cellulose acetate composition. It would appear that this substance does not assist the deformation of cellulose acetate at high rates of stressing sufficiently to compensate for reductions in fracture strength. Thus different plasticizers undoubtedly affect strength properties in different ways. In the case of low temperature impact strength an investigation of the specific effects of different plasticizers has been carried out by Gloor,[38] who found that the impact strength of plasticized cellulose acetate at − 40° F. increased as the slope of the viscosity temperature curve of the plasticizer diminished.

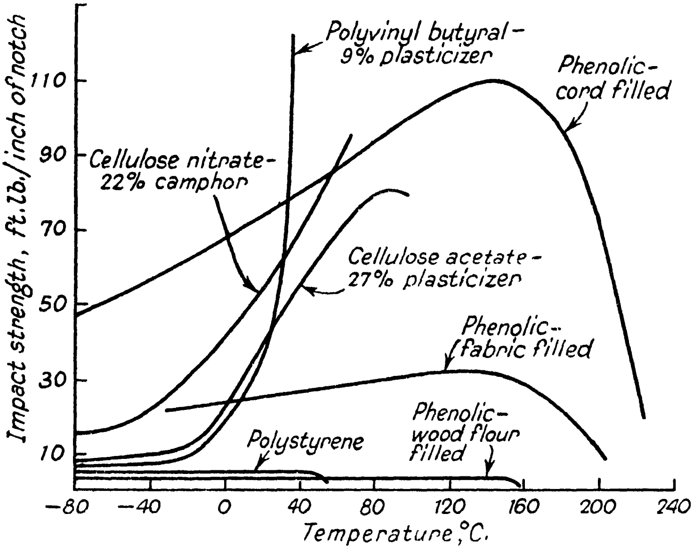


FIG. 71.—The impact strength of various plastic materials.[40]

However, it should be noted that this observed increase in impact strength with temperature is partly due to the fact that most of the plastics normally handled are already selected to have a certain rigidity. If the temperature were very greatly increased or if much higher plasticizer contents were employed, a further increase in either factor would be likely to reduce the impact strength through a reduction of the stress a force factor (*P*) of the impact product $\int P.\, d(D)$ (see p. 146). This type of behaviour is shown by polystyrene in Fig. 71.

Another consequence of the properties of the highly elastic type of deformation is that a variation of measured impact strength with the velocity of impact is common, and may occur in any velocity range. In particular, the reduction in impact strength with increasing velocity of impact (negative velocity sensitivity) is characteristic. Further, the measured impact strength may be either larger or smaller than the energy to break in slow fracture, depending on the nature of the solution of the two complicated simultaneous equations for fracture and deformation under the varying circumstances. In this connection there is a certain similarity between the highly elastic deformation of plastics and the non-ideal or "plastic" deformation of metals under impact conditions. For example, an investigation into the impact behaviour of eight metals and alloys carried out by Clark and Dätwyler[42] shows some effects similar to those assumed for plastics in the preceding discussions. They investigated both the impact strength (energy absorbed) and the force-elongation curve of their test pieces using an oscillograph technique and in this way were able to demonstrate the cause of observed changes in impact strength. The results showed that maximum stresses were always greater in dynamic than in static experiments, and that where the impact strength was less than the energy required for slow fracture this was due to a decrease in the "plastic" deformation.

Flexibility, Deformation and Brittle-point Tests

According to the preceding discussion the impact strength of most thermoplastics is largely determined by the extent to which the highly elastic deformation occurs under conditions of impact. It is, therefore, obvious that a special interest attaches to the determination of the conditions, and in particular the temperatures, at which considerable deformations of plastic materials can take place quickly. This problem has become of considerable technical interest in connection with the behaviour of rubbers under sub-zero conditions. As the temperature is lowered the rubber gradually reaches a condition where the highly elastic deformation does not easily occur and may not take place before fracture. The determination of the point where a rubber is no longer capable of fast deformation has therefore been made the basis of a number of more or less empirical flexibility tests.

For instance, Selker, Winspear and Kemp[43] have described an apparatus in which rubber samples are cooled in a bath of acetone and then subjected to quick flexure. In this way a temperature known as the *brittle point* can be determined, below which the sample is broken and above which it can be deformed without fracture. Results obtained in this way showed that the brittle point was reduced as the molecular weight of the rubber was increased. For instance, a polyisobutylene of molecular weight 1,500 had a brittle point of 23° C., and with molecular weights above 10,000 brittle points of 50·2° C. were recorded. Similarly, a polythene of low molecular weight had a brittle point at − 15° C., while a higher molecular weight material gave a value of − 68·5° C. Similar results have been obtained by Boyer and Spencer[44] using polymer fractions and mixtures of polyvinylidene chloride containing 9 per cent plasticizer (Fig. 72). Other work by Kemp, Malm and Winspear,[45] using a completely mechanical apparatus whereby the velocity and radius of flexures could be varied, has established that both these factors affect the brittle point (Table XL). Their figures suggest that the quantity $\left[\frac{d(D_{HE})}{dt}\right]_{(max)}$ plays an essential part in the brittle-point measurement.

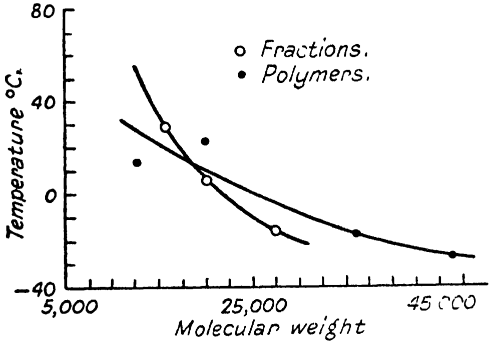


FIG. 72.—The brittle temperature of plasticized polyvinylidene chloride as a function of molecular weight.[44]

It is clear that, with these materials at a given temperature, a larger deformation may be given if it is applied slowly.

This work has been further linked to impact conditions by King,[46] who investigated the effect of bending a rubber loop slowly (1 to 1·5 sec.) and "instantaneously." The brittle-point temperatures so obtained were compared with the "shatter point" where a heavy pointed bar was dropped 3 to 5 in. on a sample placed on a flat hardwood surface and the temperature at which breakage occurred was found (Table XLI). King also found that, in general, addition of a plasticizer caused a lowering of the brittle point.

The rubbers concerned are at these low temperatures in a similar condition to that of much harder plastic materials under normal conditions, where similar effects may be expected. At ordinary temperatures the rates of deformation of two soft plastics were investigated by Haward,[8] namely: plasticized polymethyl methacrylate and cellulose acetate. In particular, he sought an explanation of the fact that the methacrylate showed much the greater extensibility and energy absorption when deformed slowly, but nevertheless had a lower impact strength, in particular giving a weaker product in laminated glass. The difference did not appear to lie in the breaking properties since the breaking time curve of the cellulose acetate could be closely imitated with the methacrylate polymer, and each gave a similar limiting fracture strength f_0 at short times. The cellulose derivatives had the advantage in taking up a greater maximum energy of Hookean elongation (9 kg. cm./sec. to 6 kg./cm./c.c.) but the energies involved were small compared with those capable of being contributed by the highly elastic process (100 kg./cm. or more). However, analysis

TABLE XL. EFFECT OF RATE OF FLEXURE AND RADIUS OF BEND ON THE TEMPERATURE OF BRITTLE FRACTURE OF CERTAIN POLYVINYL COMPOSITIONS

Speed of application of deformation	Radius of bending stress	Temperature of brittle fracture	
		Polyvinyl chloride composition	Polyvinyl chloro-acetate
r.p.m	cm	°C	°C.
150	2·54	− 32·5	− 70·5
	3·81	− 46·5	
75	2·54	− 38·5	− 72
	3·81	− 51·5	

TABLE XLI. COMPARISON OF THE BRITTLE TEMPERATURE OBTAINED BY DIFFERENT METHODS

Material	1 sec bend	Instantaneous bend	Shatter point
	° F.	° F.	° F
Neoprene I.L.S.	− 13	− 5	− 3
Plasticized polyvinyl chloride ..	− 67	− 62	− 58
Plasticized polyvinyl butyrate ..	− 49	− 8	− 4

of the rate of deformation stress curves (Fig. 73) showed that a plasticized methacrylate having a value of f_0 close to that of the cellulose acetate deformed more slowly and this difference tended to increase at higher stresses; i.e. all the evidence pointed to the possibility that $\left[\frac{d(D_{HE})}{dt}\right]_{f_0}$ max was much greater for the cellulose acetate than for the methacrylate and that this was the vital contribution to its higher impact strength. By using a low velocity pendulum and a somewhat larger quantity of plasticizer in the methacrylate it was possible to construct a tension impact experiment where the highly elastic deformation of the methacrylate did occur and a higher energy absorption was found than with the cellulose acetate. Once also, a changeover was observed with the methacrylate from tough to brittle rupture as the velocity was increased. These results are shown in Table XLII.

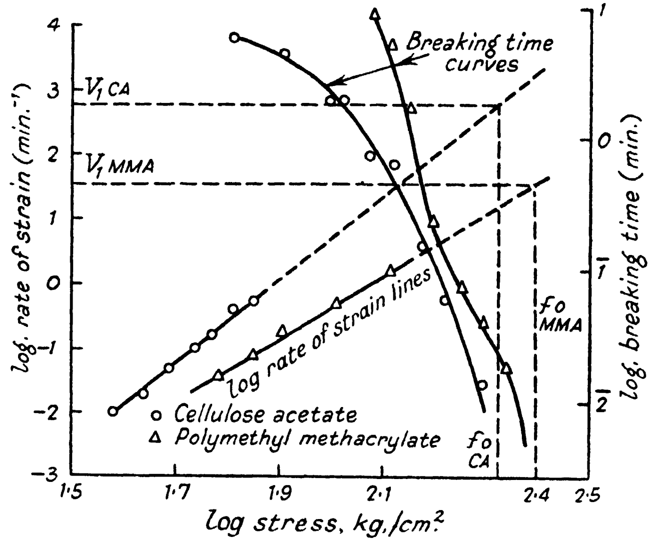


FIG. 73.—Logarithmic plots for the maximum rate of highly elastic strain and breaking times against the initial plasticized cellulose acetate and polymethyl methacrylate. It is suggested that the breaking time curves correspond with a maximum short time fracture stress and this is marked f_0. Where this stress cuts the extrapolated curve for the maximum rate of strain the maximum value of $\frac{d(D_{HE})}{dt}$ is indicated. This is higher for the cellulose acetate than the methacrylate resin.[8]

The views of Haward are in general agreement with those of

Boyer and Spencer. In two recent publications[44, 47] they define the brittle point or brittle temperature as "that temperature at which the time interval required by the sample to undergo the necessary deformation is just equal to the time interval of the test method." It will be clear that this definition is fully consistent with the views of Haward, but Boyer and Spencer give a different explanation of the effect of a variation in molecular weight. In their opinion the effect of increasing molecular weight is to increase the limiting deformation at unit stress according to the theoretical relation of Mark and Kuhn,[48] namely:

TABLE XLII. THE ENERGY ABSORPTION IN KG.CM./CM² OF MATERIALS SUDDENLY EXTENDED AT DIFFERENT VELOCITIES

Initial rate of strain	Energy absorption for material named				
	Plasticized cellulose acetate 13° C.	Plasticized polymethyl methacrylate			Celluloid 16° C.
		25% *dibutyl phthalate* 12° C.	31·5% *dibutyl phthalate* 8–9° C.	31·5% *dibutyl phthalate* 14° C.	
62 sec.$^{-1}$	160	10–20	230	—	133
93 sec.$^{-1}$	130	10–20	170	260	116
180 sec.$^{-1}$	—	—	20	260	84
250 sec.$^{-1}$	130	—	20	250	84

$$D_{HE(\infty)} = M/7\,RT\rho \text{ (where } \rho \text{ is the density).}$$

Thus raising the molecular weight raises $D_{HE(\infty)}$ and so allows a specified deformation to take place at a lower temperature. On the other hand, according to the experimental evidence presented in Chap. IV, the deformation of plastic and rubber-like materials at a given stress does not increase with molecular weight, as ordinarily understood, but rather the opposite. In their investigations on the effect of molecular weight and molecular weight distribution on the mechanical properties of a styrene-butadiene rubber Kemp and Straitiff[49] found that an increase in the molecular weight could lead to an *increase* in the measured elastic modulus by a factor as large as 4, i.e. with this material the deformation of a high molecular weight polymer by a given stress would be one quarter of that for a polymer of low molecular weight. In the author's opinion, therefore, the lowering of the brittle point brought about by the raising of the molecular weight is to be explained by the increase in the stresses at which fracture occurs, and the consequent increase in the effective values of both D_{HE} and $d\,D_{HE}/d\,t$, or more strictly the product of these quantities and the stress by amounts which more than compensate for a smaller increase in the stresses required for a given deformation. However, if by molecular weight is meant the length or weight of the free chain between cross-linkages in a highly vulcanized rubber the circumstances are very different and the same difference of interpretation does not arise.

Where the capacity of materials to deform quickly is the main feature determining their impact strength, and resistance to rough usage, the determination of the maximum velocity of deformation, or of a velocity related to it may be a good method of measuring impact strength. This point of view has been supported by Myers,[50] who developed the flywheel for making measurements on plastic sheeting (Plate XI (*b*)). In this method the velocity of the flywheel is increased until a speed is found at which five out of ten strips are broken when struck by the revolving hammer head under standard geometrical conditions (0·100 in. clearance, sheet 0·020 in. thick). It is probable that both ideal and non-ideal elasticity contribute to the result obtained by Myer's technique (as they do under impact), but the contribution of even the ideal deformations may be restricted where comparatively high velocities are used (up to 54 ft./sec.), and the forces associated with $V\sqrt{E\rho}$ will not be negligible.

The velocities measured by Myers are definitely temperature-sensitive, the increase being typically 2 to 4 times for a rise of 25° C. Myers shows that there is little relation between his velocities and the results of a notched Izod test (except apparently for materials having very low impactometer velocities) and considers that the velocity method shows the best correlation with service experience. Undoubtedly these results show up important properties of the materials but service conditions are not all the same and it may well be that flexibility (capacity to deform quickly) of plastic sheeting may be of greater importance than the energy of deformation. Myers' experiments represent a further extension of the brittle point type of deformation test to plastic materials at ordinary temperatures.

In general, the evidence obtained in brittle point measurements is clearly less complete than information about the whole stress-strain curve under dynamic conditions. Recently an increasing amount of work has been published concerning such methods of investigation in connection with the testing of metals; some of these papers have been summarized by Morey[4] but the techniques concerned have not yet been widely applied to plastic materials.

Velocity Sensitivity in Impact Strength

The impact strength of any material is a function of the velocity of testing. An example was given in Table XLII of negative velocity sensitivity, i.e. a decrease in energy absorption with increasing velocity at low rates of impact, and another, taken from the work of Callendar,[51] is given in Fig. 74. There seems no theoretical difficulty in ascribing these changes to the existence of a time-dependent deformation, though the connection is not established. However, such factors can hardly account for the *positive* velocity sensitivity occurring with the filled ebonite *C* in Fig. 74, with the various materials examined by Bailey,[1] or in the

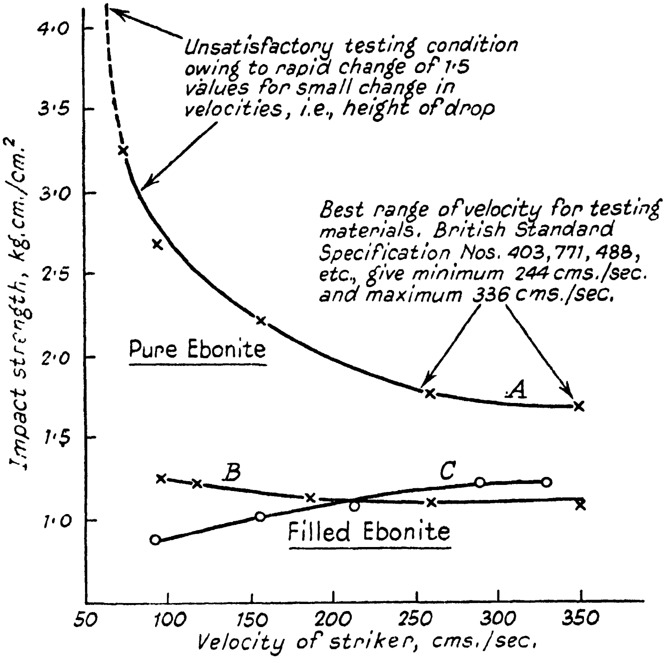


FIG. 74.—Impact strength as a function of the velocity of the striker for ebonite.[51]

filled phenolic resins investigated by Nason *et al.*[33,52] which rose from 2·3 to 3·1 ft.-lb. with a velocity increase of 10 to 60 ft./sec. The cause of such increases in impact strength with increasing velocity cannot be satisfactorily settled at the present time, but a number of possible sources of energy absorption suggest themselves:

(1) *The Time Factor* must be expected to operate in all cases where no real upper limit of fracture stress occurs, but the magnitude of the effect to be expected is necessarily somewhat hypothetical since not much is known about the variation in fracture stress with time at such short times. On the other hand it does not seem that very large changes are to be anticipated since we are dealing only with the relatively small changes in fracture time at different velocities of impact, and not with the large time differences involved in the analogy between impact and static testing.

(2) *The Weight Factor* can operate to cause positive velocity sensitivity wherever the mass of the striker is reduced for the purpose of high velocity measurements. For the theory to operate in Cox's form[9] the energy losses in the redistribution of kinetic energy on collision must be taken up *somewhere*, e.g. by deformation at the point of contact.

(3) *Frictional Effects.* Where there is an appreciable energy uptake due to tearing and frictional processes these can be visualized as taking up more energy at high velocities.

(4) *Izod Tests.* Where the experiment is so arranged that the test piece is broken at a point remote from the point of contact with the striker, vibrational factors can lead to a greater absorption of energy at high velocities. The effect of increasing the velocity of impact will be to increase the energy absorption about the point of contact with the striker, while the stresses and energy absorption round the notch or point of fracture remain the same.

(5) *Non-ideal Deformations.* Although the role of the highly elastic and other deformations in causing *negative* velocity sensitivity is emphasized, so little is known about the relations between fracture and deformation at high velocities that the possibility of effects in the opposite sense is not excluded.

In general, the only conclusion that can be drawn with regard to positive velocity sensitivity is that the factors concerned seem to be mostly of a gradual nature, and that very drastic cases of positive velocity sensitivity are hardly to be expected with simple materials. This generalization agrees with the present evidence as far as it goes.

Where plastics are largely subject to Hookean deformations we might expect them to show a negative velocity sensitivity similar to glass. To test this point some experiments have been carried out by Haward[52a] [Fig. 75 (*a*) and (*b*)]. They were made by dropping a steel ball or bolt on to a plastic square from an increasing height until fracture occurs. It will be seen that with 12 × 12 × $\frac{1}{8}$ in. Perspex squares a reduction in energy to fracture occurs in a velocity region of 1,000 cm./sec. where $V\sqrt{E\rho} = 200$ kg./cm^2., comparing with a static tensile strength of 630 to 760 kg./cm.[2,53] but that with 6 × 6 × $\frac{1}{8}$ in. squares this fall in energy to fracture only sets in at a higher velocity. The more drastic character of the effect with larger test pieces is in agreement with the experimental results for glass, and it would appear that the final working out of the mode of action of the impulsive or vibrational forces in simply supported squares will normally involve the dimensions of the test piece. At high speeds the values for the two types of

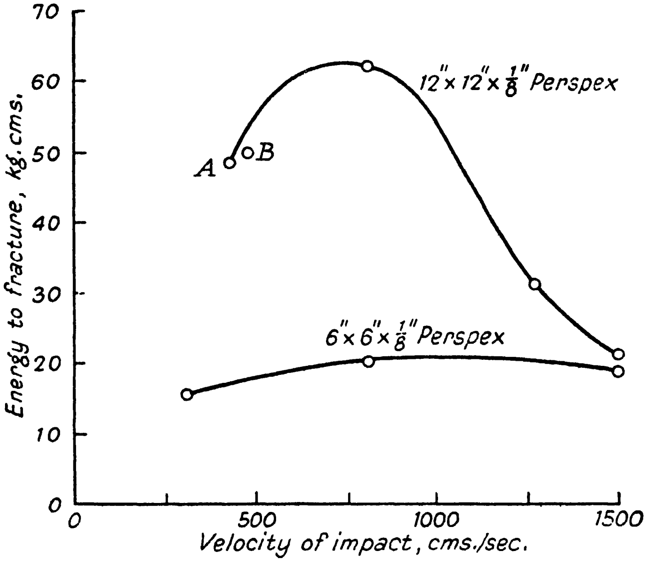


FIG. 75 (*a*).—The energy required to fracture a square of "Perspex" (polymethyl methacrylate) by a falling object. Experiments *A* and *B* were made with a heavy ball and bolt respectively, thus giving a very different radius of curvature in contact with the test piece.[52a]

square approach each other, i.e. the parts of the specimen remote from the point of impact play relatively little part in resistance to high velocity impact under these conditions. With the more brittle styrene sheet the reduction in energy to fracture sets in at lower velocities than with Perspex, and according to this method of investigation it therefore shows properties intermediate between Perspex and glass.

All these materials show some positive velocity sensitivity at low velocities, and the results emphasize that this is not a good indication of behaviour at high velocities. It follows that where a material is to be used in circumstances where high velocity impact is likely to occur the standard Izod test at 11 ft./sec. (340 cm./sec.) cannot be regarded as reliable.

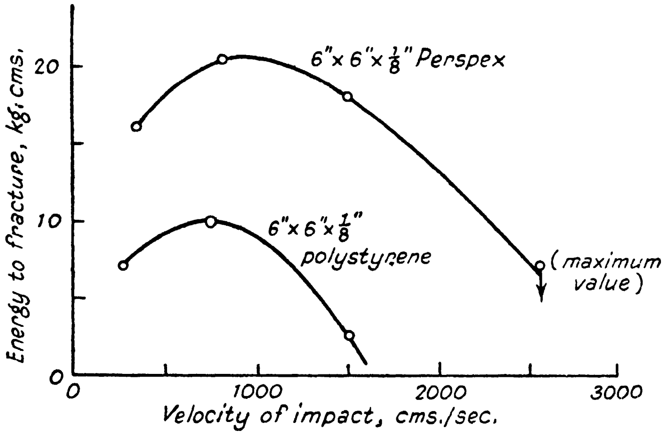


FIG. 75 (*b*).—The energy required to fracture "Perspex" and polystyrene squares.[52a]

Bullet Impact

There is little published material on the subject of bullet impact; it should be realized that bullet velocities are a factor of 10 or more above those just mentioned as high velocity impact, and that the greatest care must, therefore, be used in relating them to any data at ordinary velocities. Further, a different criterion of failure is commonly used with projectiles; a material may be regarded as having failed if it is cracked under an impact test, but with a bullet success is often judged by whether the bullet is stopped. This naturally leads to the development of specific materials. For example, two composite materials containing glass or glass-like components have been used with success, namely, certain types of laminated glass and the "plastic armour and protective plating" described by Lawrie.[54] The latter was made by incorporating 70 per cent of flint or quartzite gravel in a mixture of pitch, lime and sawdust; it was superior to steel armour plate in resistance to shell splinters at 5,000 ft./sec., but inferior, on a weight for weight basis, for splinters at 1,500 ft./sec. A laminated glass bullet-proof window capable of stopping a perpendicular impact from a ·303 in. armour-piercing bullet at 2,400 ft./sec. is illustrated in Plate XII (*a*).

The effect of a bullet on two plastics is illustrated in Plate XIII with photographs taken from the work of Axilrod and Kline for the plastics.[32] The former showed that the amount of shattering was very different with cellulose acetate and vinyl chloride-acetate copolymer. Also, in some cases the cracking effect with the cellulose acetate was interestingly larger with the lower velocity projectiles. Preston[55] has investigated bullet impact on glass and was concerned to illustrate the shattering of glass characteristic of bullet impact and to establish that bullets do not make neat circular holes through glass such as would imply rupture under shear. He showed that the hole left by the bullet was invariably surrounded by a chrysanthemum-like texture of cracks, more pronounced with thicker glass, which could be regarded as the results of superimposing radial cracks formed under bending tension on top of the Hertzian "cone" type of break.

Pendulum Impact Strength and Energy to Fracture

The distinction between the energy required just to fracture a test piece, generally referred to as the "energy to fracture," and that given as the result of a Charpy or Izod pendulum test, where separation of the broken half occurs, has already been mentioned; and Lamb[56] recognized at an early stage that the energy to fracture must be considered in relating impact experiments with the known elastic properties of materials. More recently a number of papers have been published which go further and argue that measurements of the energy to fracture constitute the best method of estimating impact behaviour under service conditions.[51, 57] This point of view is supported by the obvious consideration that a cracked article is of no further use.

A method of measuring the energy to fracture by dropping a slider on to a supported beam of a plastic material was investigated by Callender,[51] who tested the method of applying a gradually increasing blow by using 5 and 10 cm. increments in the drop on a single test piece, and comparing the results obtained in this way with those in which only a single blow was given to each test piece (Table XLIII). His figures show that this type of experimental procedure does give consistently significant results.

TABLE XLIII. IMPACT STRENGTH BY SINGLE BLOW AND INCREASING BLOW METHODS

Material	Increasing blow results		Single blow	No. of tests
	5 cm. increments	10 cm. increments		
Moulding ebonite C	0·49	0·51	0·50	40
Bitumastic composition with cotton filler A	—	0·87	0·88	30
Inferior sample B	0·39	0·41	0·42	40
Moulding ebonite D	0·57	0·62	—	20
Pure ebonite sheet E	—	1·18	1·24	70
Best filled ebonite D	—	1·29	1·32	70
Filled ebonite E	—	0·62	0·61	70

In other measurements of the excess swing type designed to estimate the "broken half" error, i.e. the energy absorbed in projecting the broken end of the test piece, both Callendar[51] and Telfair and Nason[67] employ a separate experiment with the broken end of an Izod test piece to show that the energy used up in moving it with the normal Izod test can be important, particularly with weak materials. Telfair and Nason compare the results from an ordinary Izod test with those obtained when the pendulum has only a small excess swing, i.e. when the "broken half" error is small but when the impact strength includes the energy required to tear and separate the pieces. Some of their results are given in Table XLIV.

Telfair and Nason consider that the energy to fracture method is justified by the fact that the wood flour-filled resin is found to be better than the asbestos-filled material, a result in accordance with experience.

It can be seen that a substantial case can be made out in favour of the energy to fracture test, particularly with materials of low impact strength, such as mineral-filled phenolics, and it is of interest to note that with these Hazen[6] also found that the Izod test was unsatisfactory, and that the static measurement of energy to break was borne out in use.

It would, therefore, appear advisable to consider the results of energy to fracture tests together with the ordinary notched Izod measurements in any new application of a plastic material unless there is a reason to the contrary, say, if the work required to tear the material apart must be included in the result, or if a good relation between Izod results and service conditions has already been established. However, a criticism of the experimental method used by Telfair and Nason for estimating the energy of the broken half has been advanced by Werring[58] as follows: "In the actual Izod test the broken half will owe part of its kinetic energy to the recoverable elastic energy stored up in it during deformation and this will constitute a true part of the impact strength." However, this element will be lowest with materials of low impact strength, and so the work of Callendar and Telfair and Nason seems qualitatively justified. On the other hand, by using a loaded test piece, Werring showed that the thrown end had little effect in an unnotched Izod test (with large energy absorption); with notched test pieces, although a genuine effect is undoubtedly present, it is not accurately measured by separate experiments with the broken half. Films showed that the trajectory of the thrown end depended on the way it was restrained at the bottom, as well as on the velocity of the striker.

TABLE XLIV. RESULTS OF DIFFERING IMPACT TESTS WITH MOULDED PHENOLIC MATERIALS

Method	Wood flour filled	Asbestos filled	Chopped canvas filled
	ft.-lb.	ft.-lb	
Standard Izod test	0·263	0·265	2·94
Energy to throw end	0·190	0·235	0·139
Energy to fracture by method of increasing blow	0·099	0·060	1·41
Small excess swing	0·134	0·082	2·77

Effects of Notching in Impact Tests

The use of notched specimens in impact testing has been widespread in the metal industry, and is widely accepted with plastics. Two points are well established. Firstly, the introduction of a notch always modifies and nearly always reduces the impact strength of plastic test specimens (Fig. 76). Secondly, experiments with notched test pieces give different results and may arrange materials in a different order of merit to that given by unnotched samples (Tables XLV and XLVI).[36] Lesser differences between materials may be introduced by qualitative differences in notching. From such well-established observations it is concluded that although an energy is measured each time, the various factors leading to the absorption of energy are not weighted in the same manner in the two methods.

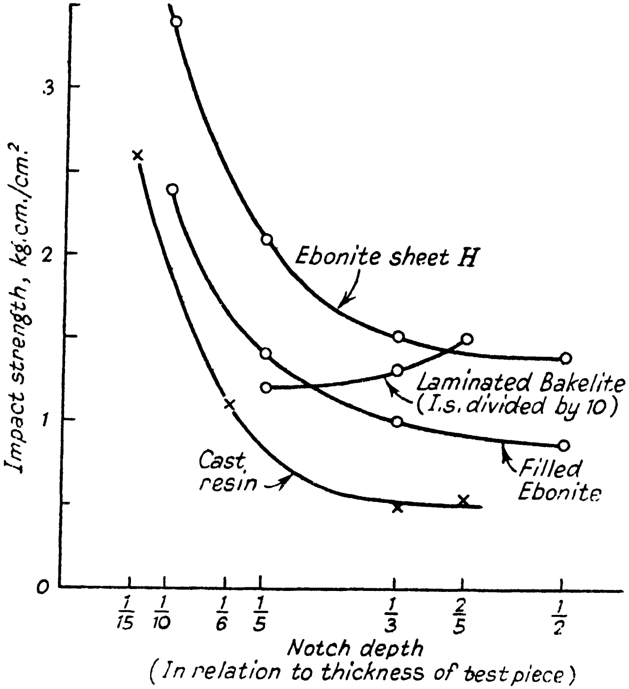


FIG. 76.—Pendulum impact strength in relation to the depth of notch.[51]

In discussing the theory of impact it is desirable to consider the simplest conditions which require us to work with geometrically simple unnotched specimens. These limitations may be serious from the practical angle, since our understanding of impact testing has not reached the point where the behaviour of a material is generally predictable. In particular, many articles in service do in fact contain points of stress concentration corresponding more to notched test pieces than unnotched ones, and experience may confirm the predictions obtained from notched bar testing rather than those given by the more simple types of experiment. Such an example is given by Burns and Werring[36] for a series of impact tests on hard rubber test pieces as used in telephone parts. The results (Table XLVII) suggest that the two notched tests are closer than the unnotched experiments to experience in use. Burns and Werring decided that the notched bar is the most valuable single test, but they also concluded that for broad application of any material requiring high impact strength the consideration of the

Table XLV. Illustrating the Lack of Relation between the Results of any Single Impact Test on Standard Test Specimens of Four Phenolic Materials and Results of Tests of the Completed Apparatus fabricated on the same Material

Material	Standard A.S.T.M. notched Izod	Unnotched bar Izod (standard A S.T.M. except unnotched)	Increasing blow, notched Izod	Increasing blow, unnotched Izod	Unnotched Charpy	Strength of telephone apparatus as determined by height of fall necessary to break
	ft.-lb.	ft -lb.	in.-lb.	ft.-lb.	ft.-lb.	
A	0·247	0·829	1·5	6·3	1·145	60
B	0·189	0·735	1·1	6·3	1·035	60
C	0·235	0·584	1·4	5·0	0·925	45
D	0·140	0·619	1·0	6·2	0·971	30

Table XLVI. Strength Relations of Three Commercial Thermoplastics

Material	Standard A.S.T.M. notched bar Izod	Unnotched bar Izod (Table III)	Increasing blow, notched bar Izod	Increasing blow, unnotched bar Izod	Unnotched bar Charpy	Flexural strength	Modulus of elasticity
	ft.-lb.	ft.-lb.	in.-lb.	in.-lb.	ft.-lb.	lb./in.^{2}	lb./in.^{2}
A	0·144	0·509	1·10	5·75	0·634	6,400	487,000
B	0·342	0·917	2·20	8·86	1·292	5,900	271,500
C	0·125	1·720	1·00	16·6	2·523	13,850	—

TABLE XLVII. STRENGTH RATINGS OF HARD RUBBER AS INDICATED BY IMPACT TESTS AND EXPERIENCE

Rating	Material	Charpy, plain. Impact	Experience rating	Material	Charpy, notched. Impact	Experience rating	Material	Izod, notched. Impact	Experience rating
		ft.-lb.			ft -lb.			ft.-lb.	
1	A	3·0	High	A	0·372	High	A	0·295	High
2	C	2·64	High	B	0·270	High	B	0·287	High
3	D	2·17	High	C	0·252	High	C	0·272	High
4	E	1·86	Medium	D	0·235	High	D	0·234	High
5	F	1·37	Medium	E	0·229	Medium	E	0·230	Medium
6	B	1·35	High	F	0·220	Medium	F	0·217	Medium
7	H	1·32	Fair	G	0·213	Medium	H	0·182	Fair
8	I	1·28	Fair	H	0·195	Fair	G	0·158	Medium
9	G	1·10	Medium	I	0·180	Fair	I	0·135	Fair
10	J	0·70	Low	J	0·154	Low	J	0·109	Low

results of more than one type of test is desirable, and, in particular, they mentioned the notched and unnotched Izod and Charpy tests, and flexural strength tests.

It is well recognized that the major effect of a notch is to cause a region of high stress concentration in the material, so that rupture is readily initiated when the stresses in the body of the plastic is well below the breaking point.

The initial stresses occurring in typical Charpy and Izod tests have been established by Coker and Filon,[59] from whose work two examples are given in Fig. 77, and these represent the state of affairs before substantial deformation takes place. The stresses are also markedly dependent on the radius of the bottom of the notch (Fig. 78) and the parallel changes in impact strength may be illustrated from the work of Callendar (Fig. 79).

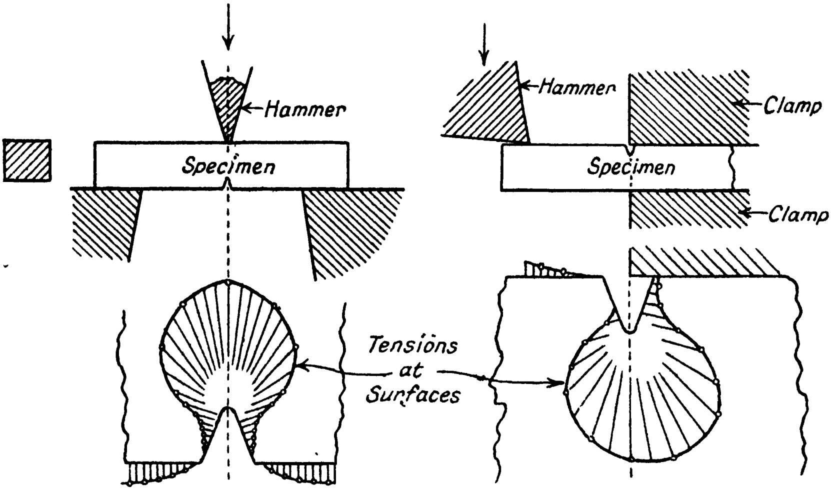


FIG. 77.—The maximum tensions in Izod and Charpy tests.[59]

At first the reason why notches generally reduce impact strength may seem clearly established, but it might be expected that the order in which materials are arranged would not be altered, and that impact measurements could never be increased. In practice, both these phenomena may be observed, though increases in impact measurements seem to be confined to certain laminated materials whose mode of rupture may be very complicated. However, apart from such exceptions, it has been shown by Shinn[60] that complex materials like laminated phenolic resins and impregnated woods are in general less notch sensitive than simple thermoplastics like cellulose acetate or polymethyl mcthacrylate.

Another general cause of difference in arrangement with notched

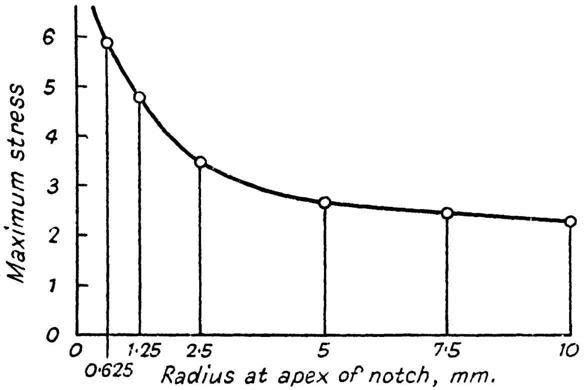


FIG. 78.—The maximum stress as a function of the radius of the notch.[59]

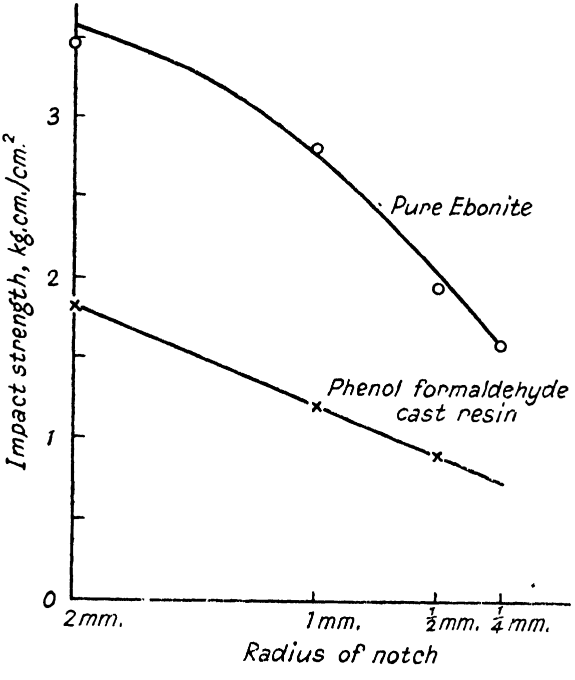


FIG. 79.—The effect of notch radius on impact strength.[51]

materials has been emphasized by Coker and Filon.[59] With ductile plastics, i.e. materials showing high values of D_{HE} and D_{visc} under conditions of impact, the influence of the notch in maintaining a high local stress will decline in the progress of the test since the radius of curvature will be increased during the deformation, but with brittle materials the high local stresses remain. According to this view the effect of deformation at a notch may be far more drastic for the behaviour of the test piece as a whole than the actual energy absorbed in the small volume concerned would suggest. In such cases no theoretical treatment of energy absorption in terms of the original shape of the test piece is valid, and this greatly increases the difficulties of predicting behaviour under impact from the known properties of a material. However, it seems to follow that where two simple materials have the same unnotched impact strength the one having the lowest modulus of elasticity (strictly speaking for short times and high stresses) should be the least notch sensitive, a conclusion in agreement with the values for the two elasticities and the impact strengths in Table XLVI. The observations by Burns and Werring[36] that the notched impact strength of methacrylate resin increases with temperature, and the unnotched test decreases, falls readily into the same picture, and agrees with the conception of notched tests giving greater weight to the deformation element which increases at higher temperature.

A further effect of the notch which may be of particular importance in the case of the irregular notches which occur in practice, has been mentioned by Alfrey.[60a] In such cases there will be a concentration of stresses along more than one axis and this will lead to further variations in fracture behaviour. Although not much is known about the behaviour of plastic materials under the action of such combined stresses in different planes there is certainly no reason to believe that the changes involved will be negligible.

Repeated Blows

When subjected to repeated blows plastic materials are broken with an energy less than that required to fracture in a single blow. That the effects concerned are not large enough to interfere seriously with the accuracy of the increasing blow "energy to fracture" test was established by Callendar,[51] who also showed that two blows at 80 per cent of the breaking energy do not seriously reduce the impact strength of various ebonites. The same problem was also investigated by Field,[61] who estimated the impact which various plastic materials would withstand "an indefinite number of times" as a fraction of the single blow impact strength (Table XLVIII).

TABLE XLVIII. IMPACT WHICH CERTAIN PLASTICS WILL WITHSTAND INDEFINITELY AS PER CENT OF SINGLE BLOW IMPACT STRENGTH

Material	Energy fraction
	%
Acrylate, injection moulded	60
Acrylate, cast	41
Polystyrene	40
Phenolic compound, compression moulded	27
Hard rubber	22
Cellulose acetate butyrate, injection moulded, different samples	3·6–10
Nylon, injection moulded	58
Phenolic laminate, paper base	50
Phenolic laminate, fabric base	45

The figures in Table XLVIII indicate the range of results to be expected, but it must be appreciated that these are likely to depend on the conditions of test. For instance, where a series of impacts are repeated very quickly the plastic is likely to be heated up, and there will be variation in its properties.

Energy Absorption without Rupture—Damping

The occurrence of non-ideal types of deformation, with the consequent degradation of kinetic into thermal energy, is of vital importance in applications where the material is liable to be exposed to sudden vibrational stresses. Here a material showing elasticity wholly or mainly of the Hookean type is liable to show resonance phenomena, leading to a vast amplification of vibrational stresses under favourable conditions, so that the article may be damaged by the resulting accumulation of energy. Where non-ideal deformations occur under low or medium stresses there will be a hysteresis loop in the stress-strain curve whose area will be a measure of the damping capacity of the material.

These properties have been discussed by de Bruyne[11] and by Lazan and Yorgiadis,[62] who emphasize the advantages of laminated plastics over steel in this respect (Fig. 80). The capacity of damping vibrational stresses has been measured by de Bruyne in terms of the *energy absorption in torsional oscillation* (Table XLIX), and

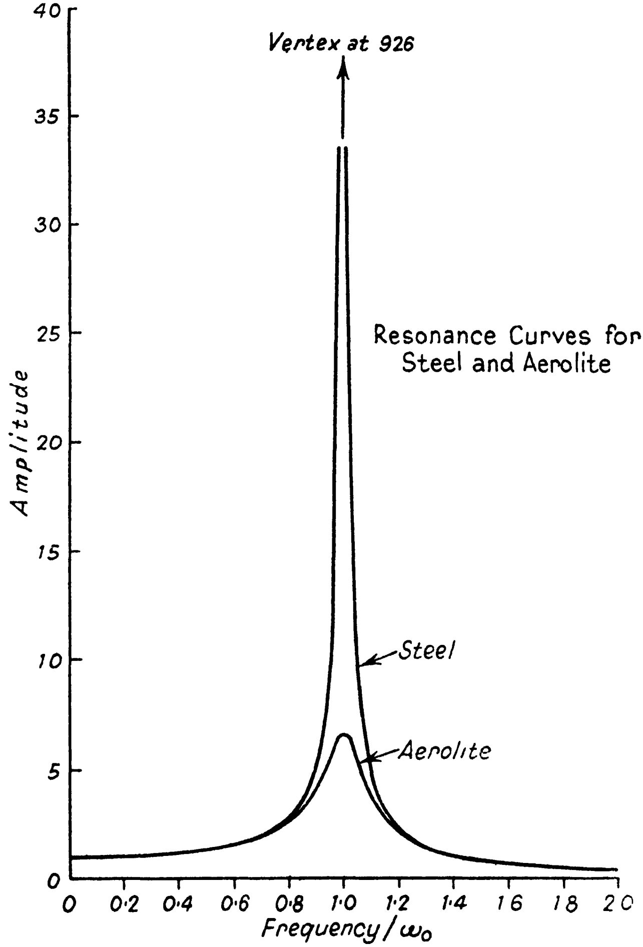


FIG. 80.—The relative behaviour of steel and a reinforced plastic ("aerolite") when subject to vibrations under resonance conditions.[11]

by Lazan in terms of a *resonance amplification factor*, i.e. the amplification of a vibrational stress under conditions of resonance; these terms are inversely related. Both workers also investigate rupture under oscillating stresses; de Bruyne shows that these stresses are not appreciably more dangerous with his plastics than steady loads, and Lazan concludes in addition that high damping capacity is not necessarily associated with low fatigue strength. Clearly these properties will also affect the transmission of shock waves through a plastic material by reducing their intensity at points distant from the point of origin, and so give rise to differences in behaviour under high velocity impact with materials having different damping capacity. This will apply particularly where fracture occurs at a distance from the point of contact with the striker.

TABLE XLIX. ENERGY ABSORPTION MEASUREMENTS FROM TORSIONAL OSCILLATION[11]

Material	Energy absorption
	%
Bakelite—fine fabric reinforcement ..	24
Bakelite—cord reinforcement	20
Bakelite—paper reinforcement	18
Mahogany and walnut	12
Zinc	11·7
Aluminium	1·1
0·9% carbon steel	0·17
Nickel	0·021

Resilience

A problem exactly opposite to that of damping is resilience, which arises particularly in the case of rubbers. It may be measured by the rebound of a pendulum which is allowed to fall on a specimen of the material in question[63] and is therefore similar to the so-called "rebound hardness" mentioned in Chap. V. If a rubber is tested initially at a very low temperature and the temperature is then raised, the resilience normally goes through a minimum where the highly elastic deformation occurs but is not readily reversed. This corresponds to the region where there is a maximum in the time factor as shown on pp. 98, 100.

REFERENCES—VI

(1) BAILEY, F. G.: *E.R.A. Report* A/T59.
(2) GEHLHOFF and THOMAS: *Z. Tech. Phys.*, 7 (1926), p. 105.
(3) KOON, A. W.: *Mod. Plast.* (September 1942), p. 88.
(4) MOREY, D. R.: *Ind. Eng. Chem.*, 37 (1945), p. 255.

(5) TELFAIR, D., NASON, H. K.: *Mod. Plast.* (April 1945), p. 145.
(6) HAZEN, T.: *Mod. Plast.* (October 1943), p. 103.
(7) MCNALLY, J. G., SHEPPARD, L. E.: *J. Phys. Chem.*, **35** (1931), p. 100.
(8) HAWARD, R. N.: *Trans. Farad. Soc.*, **39** (1943), p. 267.
(9) COX, H.: *Camb. Phil. Soc. Trans.* (1849), p. 73. See also TIMOSHENKO, S.: *Strength of Materials*, p. 303 (Macmillan, 1940).
(10) TUZI, Z., NISIDA, M.: *Phil. Mag.*, **21** (1936), p. 448.
(11) DE BRUYNE, N. A.: *Roy. Aeronautical Soc. Jnl.*, **41** (1939), p. 523.
(12) BOUSSINESQ, M. S.: *Compt. Rend.*, **97** (1883), p. 154.
(13) DONNEL, L. H.: *Trans. Amer. Soc. Mech. Eng.*, **52** (1930), APM, p. 161.
(14) TIMOSHENKO, S.: *Theory of Elasticity*, p. 389 (McGraw Hill, 1934).
(15) SAINT-VENANT AND FLAMANT: *Compt. Rend.* (1883), pp. 127, 214, 218, 353.
(16) BOUSSINESQ, M. J.: *History of Elasticity and Strength of Materials*, Pt. II, Vol. II, p. 286 (Todhunter & Pearson, 1893).
(17) MOREY, D. R.: *Ind. Eng. Chem.*, **37** (1945), p. 255.
(18) TIMOSHENKO, S.: *Theory of Plates and Shells*, pp. 76, 165, 276 (McGraw Hill, 1940).
(19) WILLIAMS, A. E.: *J. Am. Ceram. Soc.*, **6** (1923), p. 980.
(20) SCHMEER, F.: *Glastech. Ber.*, **9** (1931), p. 544.
(21) PRESTON, F. W.: *J. Am. Ceram. Soc.*, **14** (1931), p. 432.
(22) HAWARD, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 5.
(23) HOLLAND, A. J., TURNER, W. E. S.: *J. Soc. Glass Tech.*, **24** (1940), p. 46.
(24) EDGERTON, H. E., BARSTOW, F. E.: *J. Am. Ceram. Soc.*, **24** (1941), p. 131.
(25) HAWARD, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 133.
(26) BAILEY, J.: Lecture to American Ceramic Soc. (September 1938).
(27) HAWARD, R. N.: *J. Soc. Glass Tech.*, **29** (1945), p. 197.
(28) EDGERTON, H. E., BARSTOW, F. E.: *J. Am. Ceram. Soc.*, **22** (1939), p. 303.
(29) *Air Ministry Specification* D.T.D., 339A (1938), p. 3.
(30) *Beama Journal*, **42** (1938), p. 19.
(31) *A.S.T.M.*, D 256—43 T.
(32) AXILROD, B. M., KLINE, G. M.: *J. Res. Nat. Bur. Standards*, **19** (1937), p. 367.
(33) TELFAIR, D., NASON, H. K.: *Mod. Plast.* (April 1945).
(34) CARSWELL, T. S., HAYES, R. F., NASON, H. K.: *Ind. Eng. Chem.*, **34** (1942), p. 454.
(35) *Mod. Plast.*, **20** (1942), p. 88.
(36) BURNS, R., WERRING, W. W.: *Proc. A.S.T.M.*, **38** (1938), p. 39.

(37) Douglas, S. P., Stoops, W. N.: *Ind. Eng. Chem.*, **28** (1936), p. 1152.
(38) Gloor, W. E.: *Ind. Eng. Chem.*, **39** (1947), p. 1125.
(39) Bartoe, W. F.: *Aviation* (January 1943), p. 129.
(40) Carswell, T. S., Telfair, D., Haslanger, R. W.: *Mod. Plast.* (July 1942), p. 65.
(41) Delmonte, J.: *Plastics in Engineering* (Panton Publishing Co., 1943).
(42) Clark, D. S., Dätwyler, G.: *A.S.T.M.*, **38** (1938), p. 98.
(43) Selker, M. L., Winspear, G. G., Kemp, A. R.: *Ind. Eng. Chem.*, **34** (1942), p. 157.
(44) Boyes, R. F., Spencer, R. S.: *Advances in Colloid Science*, Vol. II, ed. Mark and Whitby, pp. 1–55 (Interscience, 1946).
(45) Kemp, A. R., Malm, F. S., Winspear, G. G.: *Ind. Eng. Chem.*, **35** (1943), p. 488.
(46) King, G. E.: *Ind. Eng. Chem.*, **35** (1943), p. 949.
(47) Boyer, R. F., Spencer, R. S.: *J. App. Phys.*, **16** (1945), p. 594.
(48) Mark, H.: *The Physical Chemistry of High Polymeric Systems*, p. 69 (Interscience, 1941).
(49) Kemp, A. R., Staitiff, W. G.: *Ind. Eng. Chem.*, **36** (1944), p. 707.
(50) Myers, C. S.: *Mod. Plast.* (October 1942), p. 81.
(51) Callendar, L. H.: *Brit. Plast.*, **13** (1942), pp. 445, 506.
(52) Carswell, T., Nason, H. K.: *Mod. Plast.* (July 1944), p. 125.
(52*a*) Haward, R. N.: *J. Soc. Glass Tech.*, **32** (1948), 211.
(53) *I.C.I. Plastics Technical Bulletin* No. 10 (February 1944).
(54) Lawrie, J. P.: *Chem. and Ind.* (1945), p. 261.
(55) Preston, F. W.: *J. Soc. Glass Tech.*, **11** (1927), p. 283.
(56) Lamb, E. H.: *Proc. Inst. Civ. Eng.*, **211** (1920), p. 184.
(57) Telfair, D., Nason, H. K.: *Mod. Plast.*, **20** (July 1943), p. 85.
(58) Werring, W. W.: *Proc. A.S.T.M.*, **38** (1938), p. 55.
(59) Coker, E. G., Filon, L. N. G.: *A Treatise on Photoelasticity*, p. 595 (Camb. Univ. Press, 1931).
(60) Shinn, N. A.: *Mod. Plast.*, Overseas edition (July 1945), p. 47.
(60*a*) Alfrey, T.: *The Mechanical Behaviour of High Polymers* (Interscience, 1948), p. 480.
(61) Field, P. M.: *Mod. Plast.* (April 1944), p. 123.
(62) Lazan, B. J., Yorgiadis, A.: *Mod. Plast.* (August 1944), p. 119.
(63) Mullins, L.: *Trans. Inst. Rubber Ind.*, **22** (1947), p. 235.

CHAPTER VII

SOME CHARACTERISTIC PROPERTIES OF COMPLEX MATERIALS

FUNDAMENTAL disadvantages of many thermosetting plastics lie in their relative weakness in tension and their somewhat low impact strength. These deficiencies are commonly overcome by combining them with a reinforcing material in such a way that the tension and impact properties are improved while the rigidity and permanence of the resins are retained. Such products furnish the most typical examples of the reinforced and laminated plastics. Naturally there are some very important differences in the behaviour of single homogeneous materials and those where several distinct substances are combined together to give a *complex* product.

The reinforcement of the laminated plastics has a definite structure, and the resultant materials may be highly anisotropic, so that a marked variation in all mechanical properties is to be observed depending on the direction in which they are measured. Many consequences follow from this characteristic: the theoretical analogy between tensile and bending strength will not always apply even where bending takes place in accordance with elementary theory; also variations in elasticity between bending and tension are to be expected. A few simple theoretical cases will be considered which serve to illustrate the nature of some of the problems, though the assumed conditions are not necessarily capable of precise realization in practice. However, where experimental evidence is available, it is presented.

Bending of a Rigid Composite Beam

Let us consider a rectangular beam rigidly constructed from two materials having the same bending and tensile strengths f, but with moduli of ideal Hookean elasticity E and $2E$, the beam being constructed so that the centre half consists of the stiffer material (Fig. 81). This beam is now assumed to be simply supported at the ends and broken under flexure in position A as shown. The stress is applied perpendicular to the layers, and the beam is assumed to bend rigidly in one piece according to the simple theoretical relations, so that the strain at any plane is proportional to the distance from the central plane of the beam.

Under these conditions the maximum strain in the inside beam will be half that in the outer beam, but since the elastic modulus is assumed to be twice as great the maximum stresses will in each case be the same, i.e. at the moment of rupture the inner and outer beams will break simultaneously. It follows that the normal force P required for rupture, which would be $2fbh^2/3l$ for either material alone where b and h are the breadth and thickness of the beam, now becomes equal to: The force required to break the whole assumed to be made of the outer material only *plus* force required to break the central half of the beam as it actually is *minus* the force required to give the same deformation to the central half of the beam if it were made of a material of elasticity E

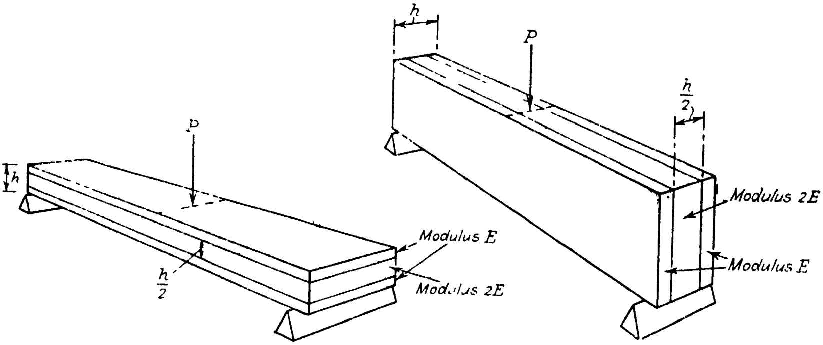


FIG. 81 POSITION A

FIG. 82 POSITION B

Illustrating the bending of a rigid composite beam.

$$= \frac{2fbh^2}{3l} \left(1 + \tfrac{1}{4} - \tfrac{1}{8}\right)$$

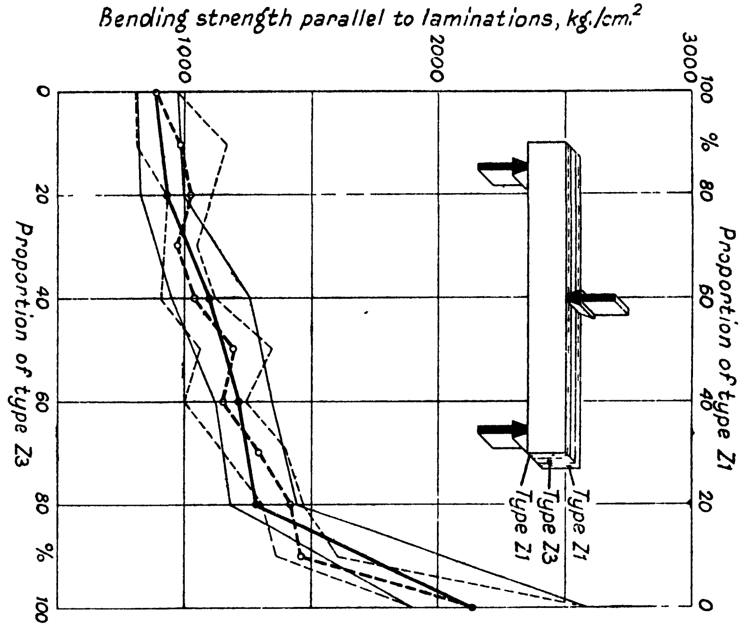
i.e. the force required to rupture and hence what would be measured as the "bending strength" of the composite beam is increased to 9/8 of that of either of the two materials broken separately.

On the other hand, if the same beam were rotated through 90° (position B) and again broken under flexure (Fig. 82), or if it were rigidly held at each end and broken under tension, the more rigid material would break first and the complex beam would be weaker than either of the two materials broken separately.

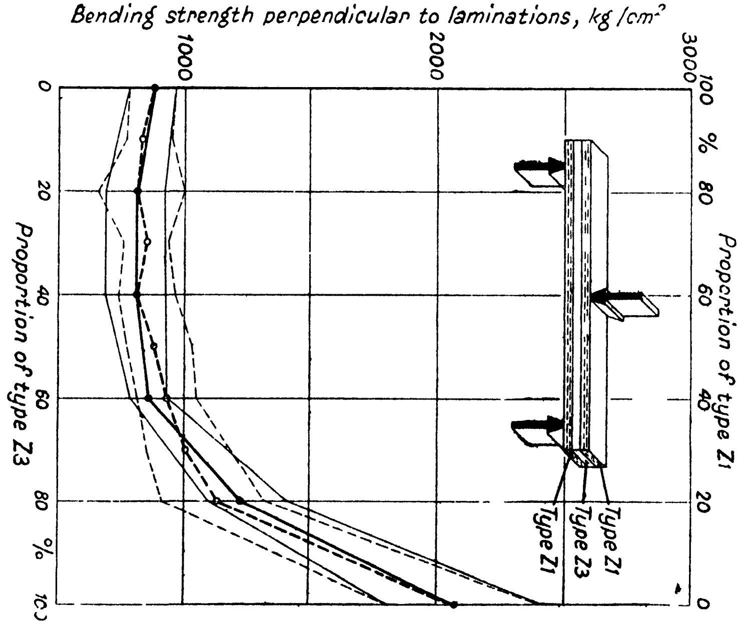
Complementary to this example is that where the two materials are assumed to have the same elasticity but different bending strengths. The deformation of the ideal rigid beam will be unaffected by the arrangement of the materials but the bending strength will depend on which of the two materials is exposed to the greater stress. Thus, if the weaker material is inside the beam will be relatively strong in bending in position A and if it is outside the beam will be weak, but if the beam is stressed in position B it will tend to be weak and will always have a strength less than the weighted average for the two materials.

Naturally few materials correspond in their properties to these arbitrary limitations, and elastic modulus and bending strength are generally found to be roughly parallel properties that cannot be independently varied. However, opportunities for testing the above theories may well exist among the many materials available. Should some materials be found where the ratio of bending strength to Hookean elasticity is constant we should expect approximately average values of the bending strength to be measured for laminated beams in position B.

The above theories are at present without direct experimental backing, but some experiments with composite plastic beams have been carried out by Jacobi,[1] which illustrate some of the phenomena concerned, although no measurements were made on the elasticity of the materials. Jacobi took a laminated beam made of two materials and investigated the strength in different positions as a function of the proportion of each constituent in the beam (Fig. 83). It will be seen that when the stronger material is on the outside of the beam the results in position A [Fig. 83 (*d*)] are above the average line for proportionality between strength and composition while the opposite occurs when the weaker material is outside [(Fig. 83 (*b*)]. In the B position [(Fig. 83 (*a*) and (*c*)] the measured strengths are always less than would correspond with linear dependence. But with a different combination of materials Jacobi obtained results much closer to proportionality in position B, as would be expected if the materials had similar ratios of bending strength to elasticity (or similar deformations at break); however, he found that these beams when broken in position A gave results generally similar to those shown in Fig. 83 (*b*) and (*d*).


Bending strength parallel to laminations, kg./cm.^{2}
1000
2000
3000
0
20
40
60
80
%
100
Proportion of type Z3
100
%
80
60
40
20
0
Proportion of type Z1
Type Z1
Type Z3
Type Z1

B


Bending strength perpendicular to laminations, kg /cm^2
1000
2000
3000
0
20
40
60
80
%
100
Proportion of type Z3
100
%
80
60
40
20
0
Proportion of type Z1
Type Z1
Type Z3
Type Z1

A

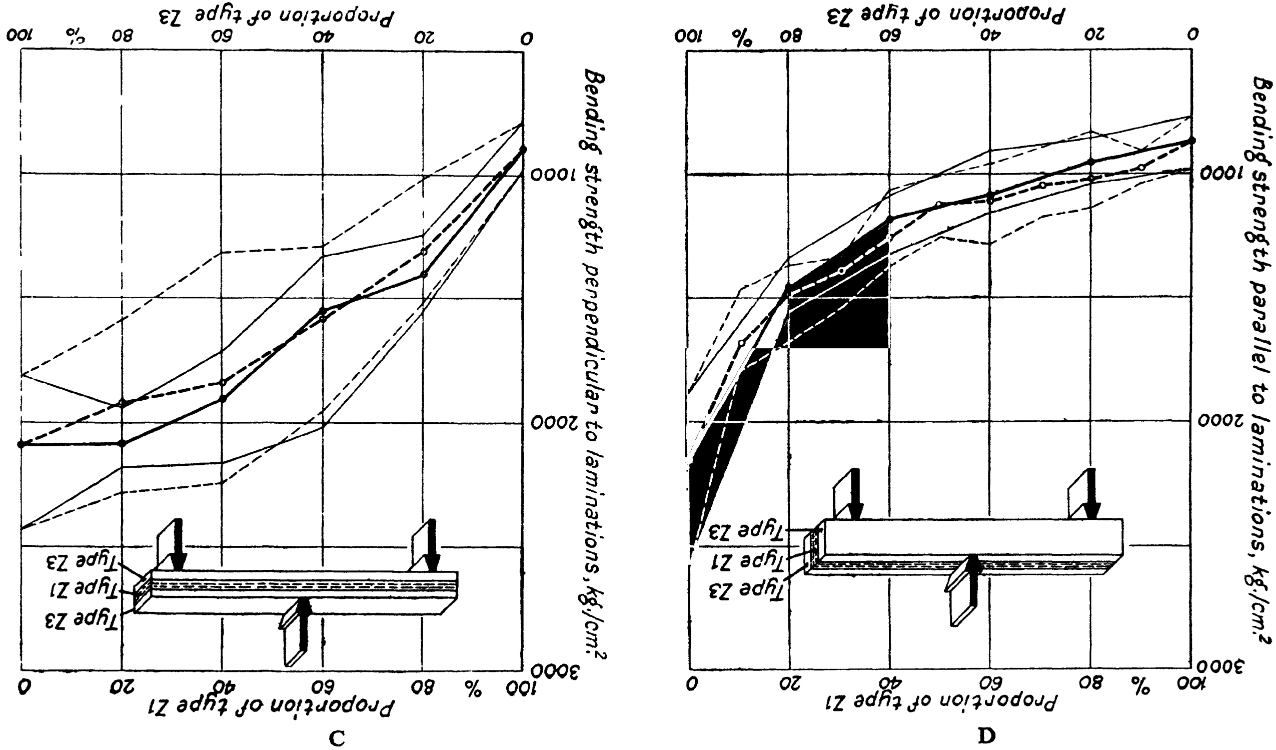


FIG. 83.—The bending strength of composite beams. "In these tests the upper and lower faint lines represent maximum and minimum values and the heavy lines the average of a number of tests."[17]

Behaviour of a Beam consisting of a Rigid Solid joined by a thin adhesive layer of a softer Material

This problem is considered solely in relation to the A position (Fig. 81) with the thickness of the inner layer initially neglected. We can consider an extreme example where the inner layer behaves in a relatively rigid manner, or another where it behaves as a liquid that allows the inner surfaces of the outer beams to slip freely in relation to each other.

(1) If the interlayer is thin and relatively rigid the whole will behave as if it were made of the outer materials alone.

(2) If the interlayer is so soft that it allows for the free motion of the two outer sections the beam will deform as if it were two separate beams of half the thickness and will bend according to the relation

$$\text{deformation} = \tfrac{1}{2}\,\frac{P\,l^3}{4\,E\,b\,(h/2)^3} = \frac{P\,l^3}{E\,b\,h^3}$$

where h is the total thickness and b the width of the composite beam.

Further, since the bending strength involves h^2 the beam with the softer inner layer will be weaker and the theoretical variation in the bending strength will be from f to $f/2$.

Experimental evidence is available for laminated glass beams of this type, whose deformation has been measured by Haward.[2] Results obtained for the bending of beams contained a cellulose acetate (hard) and vinyl butyral (soft) interlayer and the results were compared with simple glass beam samples of varying lengths (Table L).

These results show that with the stiffer interlayer the beam bends approximately as a whole, giving an elastic modulus close to that of sheet glass, but with the softer vinyl interlayer the apparent modulus of the beam is reduced. If we allow for the thickness of the interlayer the apparent modulus would be expected to fall to 142,000 kg./cm.^{2} for both beams bending separately—a prediction in good agreement with the observed results. However, it is clear that complete freedom of movement for the two sections of the beam occurs only with short beams, even with vinyl interlayer, and it seems probable that larger deformations of the interlayer are required with the longer beams for full independence of the upper and lower parts, so that stresses are set up which restrict the freedom of movement of the upper and lower halves.

Theoretical complications are introduced into the bending strength of laminated glass, because where both sections of the beam are stressed there is a greater probability of one of them containing a particularly weak flaw. This problem is analogous to that of the strength-area relation considered by Bailey (Chap. III).

TABLE L. "YOUNG'S MODULUS" IN BENDING FOR GLASS AND LAMINATED GLASS BEAMS

Material	Length of beam	Width	Thickness	E i.e apparent modulus from bending equation
	cm	cm.	cm.	kg./cm ^{2}
Sheet glass	60	2·55	0·397	730,000
	45	2·55	0·397	700,000
	30	2·55	0·397	690,000
Acetate laminated glass ..	90	2·55	0·473	690,000
	60	2·55	0·473	720,000
	45	2·55	0·473	680,000
	30	2·55	0·473	670,000
Vinyl butyral laminated glass	90	2·45	0·434	480,000
	60	2·45	0·434	360,000
	45	2·45	0·434	310,000
	30	2·45	0·434	240,000
	22	2·45	0·434	190,000
	16	2·45	0·434	170,000

However, it can safely be predicted that the bending strength of laminated glass with the softer interlayers is likely to be less than with harder interlayers, and this is in agreement with the figures given by Watkins[3] which place the bending strengths in the order of the elastic constants of the interlayers (Table LI). Some ambiguity surrounds the term "elastic constants" here, but the differences are so large that the right arrangement of the materials

TABLE LI. BENDING STRENGTH OF PLATE GLASS AND LAMINATED GLASS HAVING DIFFERENT TYPES OF PLASTIC INTERLAYER

Material	Bending strength
	lb./in.^{2}
Plate glass	7,500
Celluloid laminated plate	6,500
Cellulose acetate laminated plate	6,000
Vinyl butyral laminated plate	5,000

would be obtained with the most approximate methods of measurement.

Some experiments carried out by the author on cellulose acetate and polyvinyl butyral laminated glass beams ($\frac{3}{16} \times \frac{3}{4} \times 12$ in.) suggested that the difference in bending strength could be rather larger than that found by Watkins; it was found that the cellulose acetate glass gave a value of 6,500 and the polyvinyl butyral only 4,500 lb./in.^{2}

Expanded Plastics

If two separated beams are conceived to deform as if connected by a rigid material their resistance to deformation will increase as their distance apart is increased. So, where rigidity and lightness are desired the existence of air pockets within a body may be of help so long as the material continues to move as a single piece. For certain special purposes, therefore, the so-called expanded plastics of cellular structure have been developed [Plate XIV (*b*)]. To give an improved surface and a further increase in rigidity they may be veneered with plywood, asbestos sheet or other plastic materials[4] [Plate XIV (*a*)]. The low density, high strength/weight ratio, and rigidity of such products gives them particular importance in aircraft construction, but they have a number of other properties useful in other applications, such as low thermal conductivities and permanent buoyancy. The mechanical properties of these materials depend on the resin used, expanded polyvinyl formal being generally stronger than phenolic or polystyrene products. However, polystyrene can be used at the lowest densities, and values of $\rho = 0{\cdot}02$ to $0{\cdot}03$ have been obtained with this resin.[5]

The best known light material is Balsa wood, which was used, together with birch plywood, in the Mosquito aircraft. However, according to Rheinfrank and Norman,[6] the U.S. Army Air Force considered wood a marginal material for combat aircraft under extreme weather conditions, and they showed that suitable properties can also be obtained with various expanded and reinforced cellulose derivatives. Core materials with a honeycomb type of structure have been used for the low density constituent, and these are claimed to give a good combination of lightness and rigidity.[7] Naturally, the development of these and other materials for special purposes render a proper understanding of their application the more important, especially in aircraft engineering.[8]

On the more theoretical side Garrard[9] has recorded the variation in tensile and compressive strength of expanded ebonite with the

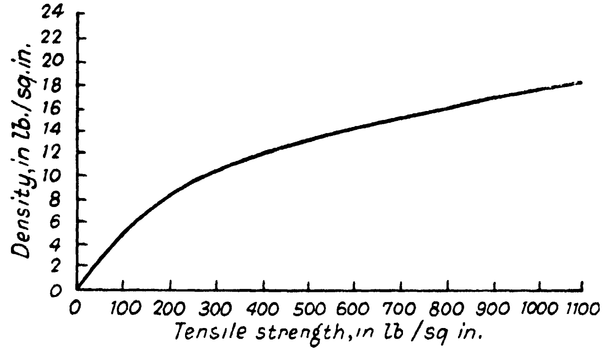


FIG. 84.—A tensile strength density curve for expanded ebonite.[9]

density (Figs. 84 and 85). He deals also with the important subject of the behaviour of these expanded materials in compression. With a short test piece the true compressive strength of the material is the only relevant factor, but with the longer columns,

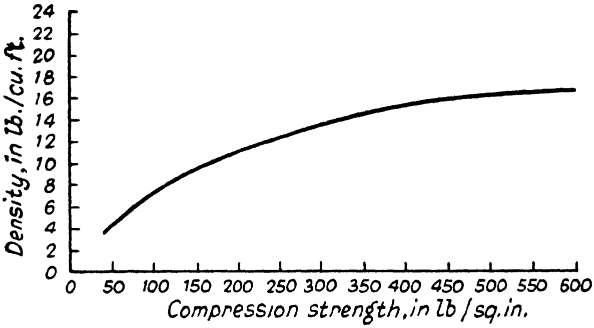


FIG. 85.—Density—compressive strength curve for expanded ebonite.[9]

which frequently occur in practice, the part may fail from buckling before its real compressive strength is approached.

The designer is therefore faced with the problem of constructing a column with its materials so distributed that failure in buckling and compression occur together; in aircraft the structure must be light. For this purpose a sandwich assembly may be used, in which the more rigid skin material is separated and supported by a low density core; such structures may endure much greater stresses than are practicable without the expanded supporting material. Comparison of the behaviour of these expanded products and other similar materials may be facilitated by the use of a "structure loading coefficient," which is the square root of the load divided by the length of the column. Allowance for density may be made by dividing compressive strength by specific gravity and expressing the result as a length (specific compressive strength). Some wood and metallic materials are compared in this manner in Fig. 86, which illustrates the value of the lightweight Balsa wood at low structure loadings, even when no skin material is used.

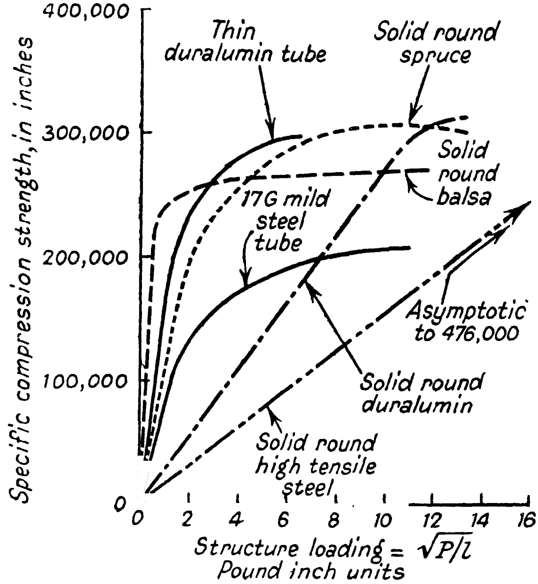


FIG. 86.—The behaviour of various light and rigid arrangements in compression.[9]

Laminated and Reinforced Plastics

This brief survey of the properties of composite beams and expanded plastics serves to illustrate the directional properties in an assembly having a regular structure. That such effects are not confined to cases where the structure is on a macroscopic scale is shown by the behaviour of metal crystals whose mechanical properties depend on the direction of tension or shear with respect to the axes of the crystal.[10] It is, therefore, not surprising to find that similar marked directional variations are also characteristic

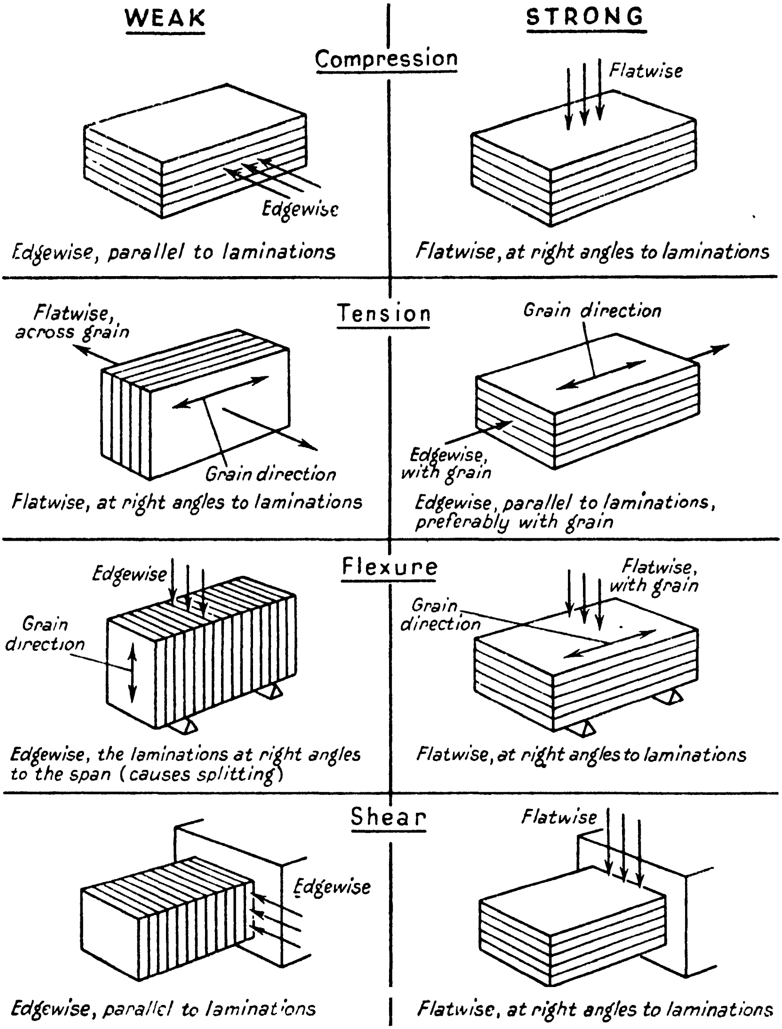

WEAK
STRONG
Compression
Flatwise
Edgewise
Edgewise, parallel to laminations
Flatwise, at right angles to laminations
Tension
Flatwise, across grain
Grain direction
Grain direction
Edgewise, with grain
Flatwise, at right angles to laminations
Edgewise, parallel to laminations, preferably with grain
Flexure
Edgewise
Grain direction
Flatwise, with grain
Grain direction
Edgewise, the laminations at right angles to the span (causes splitting)
Flatwise, at right angles to laminations
Shear
Edgewise
Flatwise
Edgewise, parallel to laminations
Flatwise, at right angles to laminations

FIG. 87.—Weak and strong positions for laminated plastics.[11]

of the laminated plastics, and it is of great importance in design to arrange for the maximum stresses to operate along the lines of greatest reinforcement (Fig. 87).[11] It is also necessary to know the type of structure on which the plastic is based, since this need not always be of the straightforward laminated type.

Sometimes it is desirable to arrange for a high proportion of the reinforcement to lie in a single direction. For example, de Bruyne[12] describes certain phenolic and cresol resins filled with a continuous cord reinforcement, with 90 per cent of the reinforcement in the warp, which he calls "aerolites" and which have greatly improved properties in their most favourable direction. Between these two extremes many intermediate forms exist, having varying degrees of reinforcement along two out of three rectangular axes. Also, many articles can conveniently be moulded directly from resin-impregnated canvas or similar materials giving products where the orientation in the reinforcing elements is confined to that brought about in the moulding process.

Mechanical Properties of the Laminated Plastics

A great deal of material has recently been published in the U.S. and elsewhere concerning the mechanical properties of commercial and experimental laminated plastics,[11, 12, 13, 14, 15, 16, 17, 18] and typical figures are given in Tables LII and LIII.[11]

A more complete tabulation of published results has recently been made by Yarsley,[19] but Table LII serves to illustrate many of the differences obtained with different types of reinforcement. In particular, the main advantage of the fabric over the paper laminates lies in improved impact and bending strengths, and it is probable that both these properties depend on increased deformability under the highest stresses. This is in general agreement with the work of Barber,[20] who made a specific comparison of various phenolic paper laminates with a fabric-filled material. Naturally, actual figures largely depend on the particular types of fabric or paper reinforcement employed, and the best products in each type may be superior to the average. For example, Barber claims that with certain types of paper reinforcement, namely: Mitscherlich sulphate and sulphate Kraft papers, increased values of the tensile strength, up to 30,000 and 21,000 lb./in.^{2} respectively, are obtained, and values of 19,000 to 28,000 lb./in.^{2} for the ultimate tensile strength of high strength paper laminates have also been given by Field.[13] Such figures suggest a considerable improvement on those observed by Caldwell (Table LII).

Table LII. Mechanical Properties of Phenolic Laminates

Base material	Tensile strength lb./in.^{2}		Modulus of elasticity tension C × 10^6		Compressive strength lb./in.^{2}		Modulus of elasticity, compressive, × 10^5		Impact strength, Charpy method, ft.-lb./in. Unnotched, ½ in. thick				Bond strength, lb., sample 1 × 1 × ½ in.
	With grain	Across grain	With grain	Across grain	Flatwise	Edgewise	Flat-wise	Edge-wise	Flatwise with grain	Flatwise across grain	Edgewise with grain	Edgewise across grain	With grain
Asbestos fabric ..	12,000	11,000	1·3	1·3	49,000	21,000	7	5	12·3	11·5	9·8	8·5	1,100
Asbestos paper ..	13,000	10,000	1·0	0·8	41,000	10,000	6	5	5·5	4·2	3·5	3·1	900
Kraft paper	16,000	11,000	1·7	1·1	38,000	21,000	7	8	8·9	4·8	6·6	4·5	1,000
Absorbent paper ..	11,000	8,000	1·0	1·0	31,000	18,000	6	6	4·5	3·4	4·5	3·5	950
Absorbent paper ..	8,000	6,000	0·9	0·7	22,000	8,000	6	5	7·2	6·5	7·5	6·4	1,100
Absorbent paper ..	13,500	10,500	1·0	1·0	36,000	21,000	7	6	3·3	4·1	3·5	4·8	950
Fine weave fabric ..	13,000	9,500	1·0	0·7	38,000	22,000	6	6	10·4	9·8	8·6	7·8	1,600
Fine weave fabric ..	14,500	10,000	1·0	0·8	40,000	22,000	6	6	15·4	10·9	10·3	9·1	1,600
Medium weave fabric..	13,000	12,000	1·0	1·0	40,000	20,000	6	6	13·2	16·0	10·0	11·5	1,700
Coarse weave fabric ..	10,000	11,000	1·0	0·8	40,000	23,000	5	5	15·8	15·5	12·0	11·7	1,800
White paper core ..	13,000	9,000	1·8	1·6	43,000	22,000	18	24	4·9	3·1	2·5	2·0	800

Data: Caldwell, L. E., *Modern Plastics*, 21 (1943), pp. 86–7.

TABLE LIII. MECHANICAL PROPERTIES OF PHENOLIC LAMINATES

Base material	Flexural strength lb./in.^{2}				Shear strength lb./in.^{2}			
	Flatwise with grain	Flatwise across grain	Edgewise with grain	Edgewise across grain	Flatwise with grain	Flatwise across grain	Edgewise with grain	Edgewise across grain
Asbestos fabric	25,000	24,000	24,000	24,000	12,000	12,000	12,000	12,000
Asbestos paper	25,000	18,000	23,000	17,000	7,500	6,400	9,700	7,900
Kraft paper	27,000	20,000	27.000	20,000	9,000	9,500	9,000	9,000
Absorbent paper . . .	17,000	18,000	14,000	15,000	7,000	7,000	7,000	7,000
Absorbent paper . . .	13,000	11,000	13,000	11,000	6,000	7,000	7,000	8,000
Absorbent paper . . .	15,000	12,500	16,000	12,500	6,000	7,500	7,500	8,500
Fine weave fabric . . .	20,000	19,000	21,000	18,000	11,000	11,000	11,000	10,000
Fine weave fabric . . .	21,000	19,000	21,000	18,000	11,500	11,500	12,000	11,000
Medium weave fabric . .	21,000	20,000	21,000	20,000	10,000	10,000	10,000	10,000
Coarse weave fabric . .	20,000	20,000	20,000	21,000	11,000	12,000	11,000	11,000
White paper core . . .	11,200	10,600	16,800	12,100	8,000	8,400	9,300	8,600

Data: CALDWELL, L. E., *Modern Plastics*, **12** (1943), pp. 86–7.

Fundamental Properties of the Laminated Plastics

Measurements for different materials simply presented in table form, though valuable as a practical guide in the present state of knowledge, give only a limited insight into the basic properties of the reinforced plastics, and of the factors limiting their possible development and application. A more fundamental approach is given in papers where the properties of the materials are dealt with in a more systematic way. One of the first was that of de Bruyne,[12] who showed that the major effect of his filler, which was mainly unidirectional, was to raise the tensile strength of a cresol resin from *ca.* 5,000 to *ca.* 26,000 lb./in.^{2} in the direction of reinforcement. On the other hand, the compressive strength remained largely unaffected round 24,000 lb./in.,^{2} though the apparent mode of rupture of the reinforced material in compression developed the form of an obvious shear (Plate XII (*b*)). The failure of laminated and other plastics under shear at angles approaching 45° to the line of compression is often a possible explanation of compressive

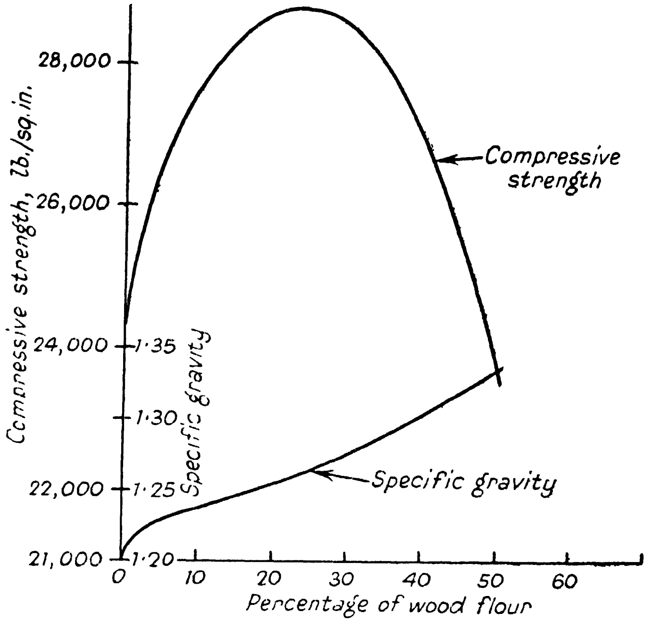


FIG. 88.—The compressive strength and specific gravity of wood flour-cresol plastics.[11]

strength (Chap. II), but this viewpoint is seldom so strikingly confirmed by the form of failure as in this example. De Bruyne's paper illustrates the effect of increases in the moulding pressure in giving improvements in tensile strength and in raising the modulus of elasticity. He also investigated the effect of the percentage of wood flour on the compressive strength and specific gravity of cresol resins (Fig. 88).

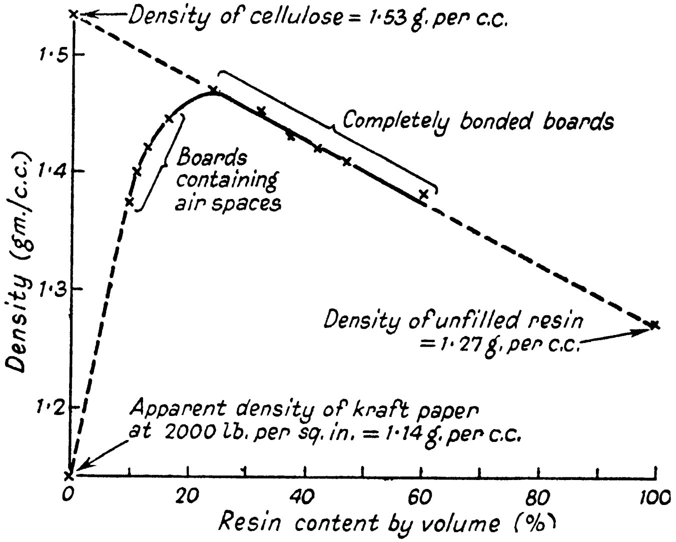


FIG. 89.—The specific gravity of a paper-reinforced phenolic resin.[22]

Some fundamental experiments have been carried out on paper base plastics by Pepper, Cox and Barwell,[21, 22] who concluded that the strengths obtainable with these materials were limited by the proportion of the stronger component present (the paper), and by the need to fill up all the "voids" or spaces therein, with the phenoplast. A considerable variety of evidence was presented in support of this theory. In the first place they investigated the specific gravity of laminates made up with different percentages of resin at the same lamination pressure, and gave results of the form shown in Fig. 89. Where all the spaces in the paper were filled the density of the laminate fell on the straight line connecting the density of the pure resin with the estimated true density of cellulose, but where the amount of resin was too small to fill up the voids, under the conditions of fabrication, lower values of the specific gravity were found. Thus, the filling of the voids here first occurred at a resin content of just over 20 per cent, and it was shown that the maximum values of the tensile strength and the modulus of elasticity were reached with materials of the same composition as shown in Figs. 90 and 91. Simultaneously, the compressive and shear strengths reach their maximum values, i.e. those of the pure resin.

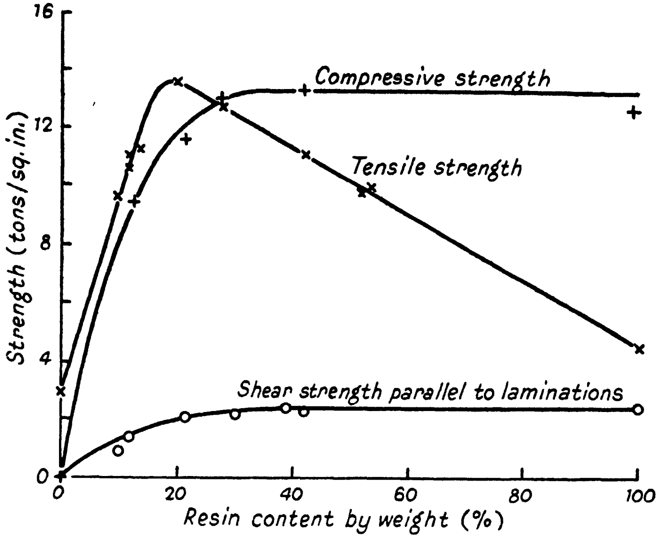


FIG. 90.—The static strength properties of a paper-reinforced phenolic resin.[22]

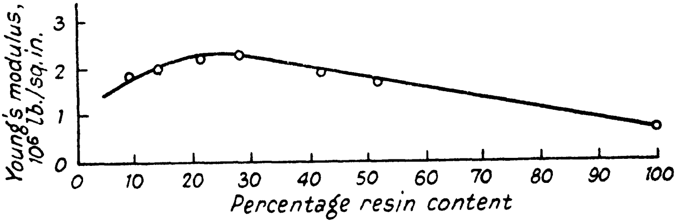


FIG. 91.—The elastic modulus of a paper-reinforced phenolic resin.[22]

Further experiments were then carried out by the same workers on the effect of pressure on a paper laminate containing 42 per cent of phenol-formaldehyde resin. It was shown that the density increases to a maximum as the pressure is raised; from such density changes the percentage of voids can be estimated, assuming a fully densified material at the highest pressure (Fig. 92). With this procedure again, strength changes follow changes in density (Fig. 93), and no improvements in strength are obtained at lamination pressures above those required to fill up the voids completely. These results are confirmed generally by Nelson[23] and Field.[13]

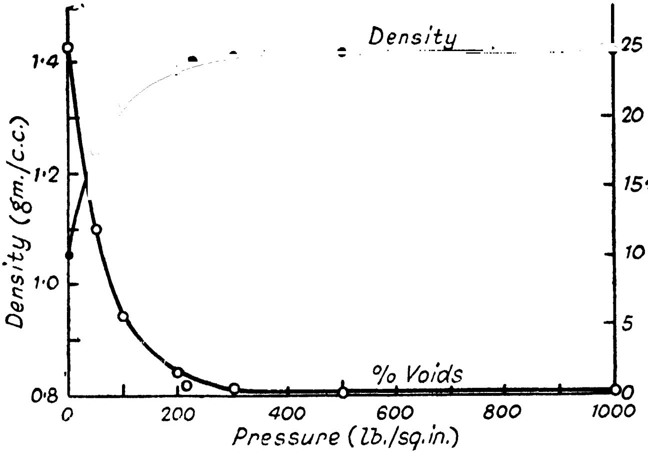


FIG. 92.—The effect of laminating pressure on the density of a paper-filled phenolic resin.[22]

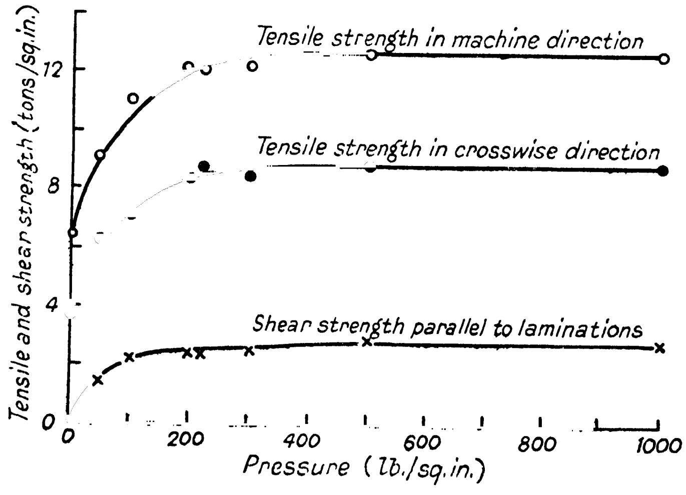


FIG. 93.—The effect of laminating pressure on the static strength of a paper-reinforced phenolic resin.[22]

Nelson also found that the tensile strength values rose to a maximum with increasing pressure and went on to show that different resins gave varying results under this type of treatment (Fig. 94). He concluded that the liquid phenolic resin was most suitable for low pressure laminates, a conclusion in general agreement with the theory of voids. The work of Field specifically supports the results of Cox and Pepper on the effect of the moulding pressure on specific gravity, and may in this respect be considered to have anticipated their investigation. He also gives a number of results illustrating the effect of the moulding pressure on mechanical properties in general agreement with those of Pepper, Cox and Barwell, though presented in a more approximate form. The existence of a pressure above which the strength and specific gravity of paper laminates do not appreciably increase may therefore be regarded as comparatively well established.

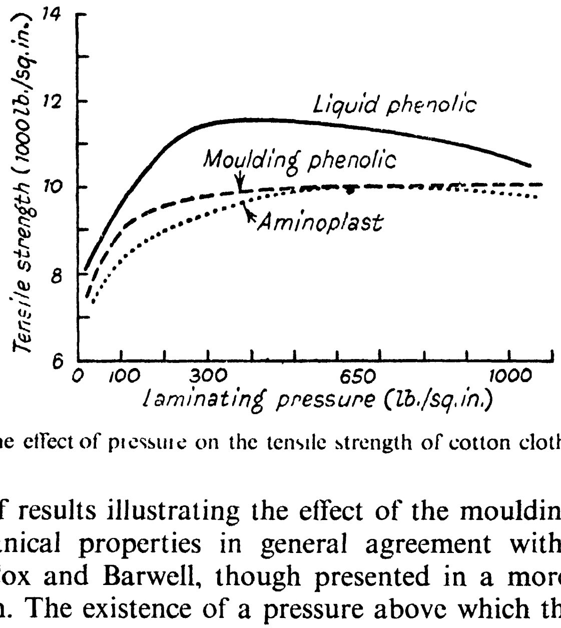


FIG. 94.—The effect of pressure on the tensile strength of cotton cloth laminates.[23]

As with other plastics, the laminated phenolic materials are susceptible to changes in humidity, and Cox and Pepper[21] used this quality to furnish further evidence for their theory of voids (Fig. 95). Their results showed that the percentage water absorption with varying composition fell sharply around a 20 per cent resin content, and that there was a parallel change in the observable loss of compressive strength on immersion in water. A reduction in static strength properties appears to be a general consequence of the action of water or dampness on paper laminates as with other plastics, even if the paper is conditioned before lamination. For instance, Croup[24] investigated the effect of subjecting the impregnated paper to varying humidities before assembly, and found that increasing humidity also caused a decrease in tensile strength and elasticity, though there was an increase in impaet strength. But he reported that the action of water vapour on thc finished laminated plastic gave a maximum value of the tensile strength at 50 per cent r.h. and a continuous increase in the impact strength. Some doubt must be felt as to whether the occurrence of a maximum tensile strength under such treatment is general since Brown[14] has quoted figures indicating a steady *decrease* in tenacity with increasing humidity.

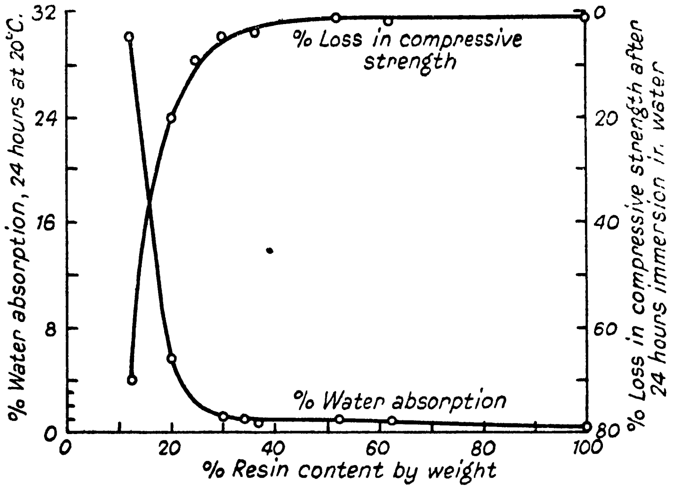


FIG. 95.—The effect of resin content on the water absorption of paper laminate.[21]

Recently, Barwell, Pepper and Hale have investigated the fabric base plastics,[25] and they consider that their results are, to a first approximation, in agreement with the theory of voids. However, they found, despite the existence of a limiting density (an implication of complete densification), that the densities of apparently fully bonded laminates still lay below the calculated values assuming no voids. It was, therefore, concluded that increasing pressure did not, within the range examined, eliminate voids completely—a result in agreement with the further observation that fully bonded boards containing a resin content of 50 per cent give an increase in density on immersion in water, whereas the density of cellulose decreases when swelling takes place in water and the resin is unaffected. Both the tensile strength and the modulus of elasticity (stiffness) of apparently fully bonded boards showed a maximum, the shape of the two curves having an interesting similarity (Figs. 96 and 97). However, the fabric base materials showed the

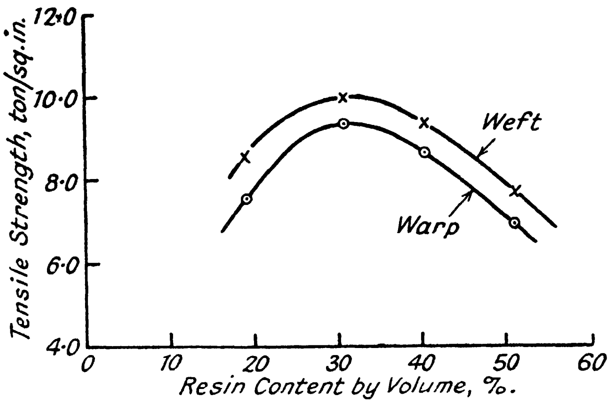


FIG. 96.—The tensile strength of fabric laminates.[25]

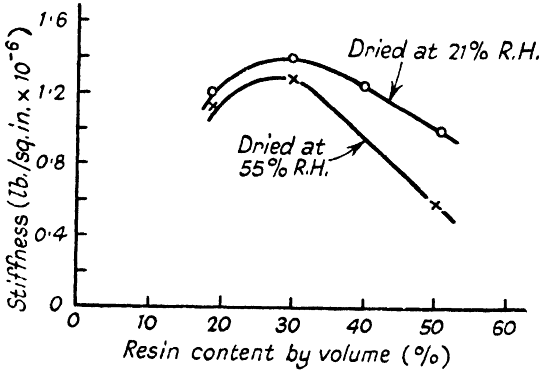


FIG. 97.—The stiffness (elastic modulus) of fabric laminates.[25]

greatest difference in behaviour to the paper impregnates in the shear strength parallel to the laminations. With the fabric base boards this type of shear strength was proportional to the resin content, while that perpendicular to the laminations was constant (Fig. 98). There was also a similarity between shear strength parallel to the laminations and compressive strength measured with the load parallel to the laminations. The latter was also directly proportional both to the resin content (Fig. 99), and to the shear strength parallel to the laminations. These results present a further analogy between shear and compression. It may also be concluded from these experiments that the threads make little or no contribution to the shear strength parallel to the laminations.

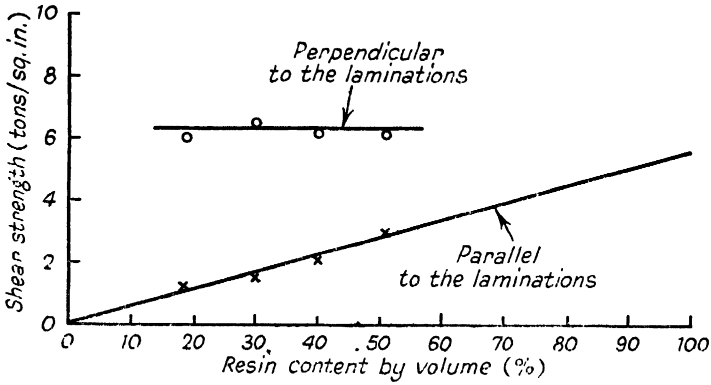


FIG. 98.—The shear strength of fabric base laminates.[25]

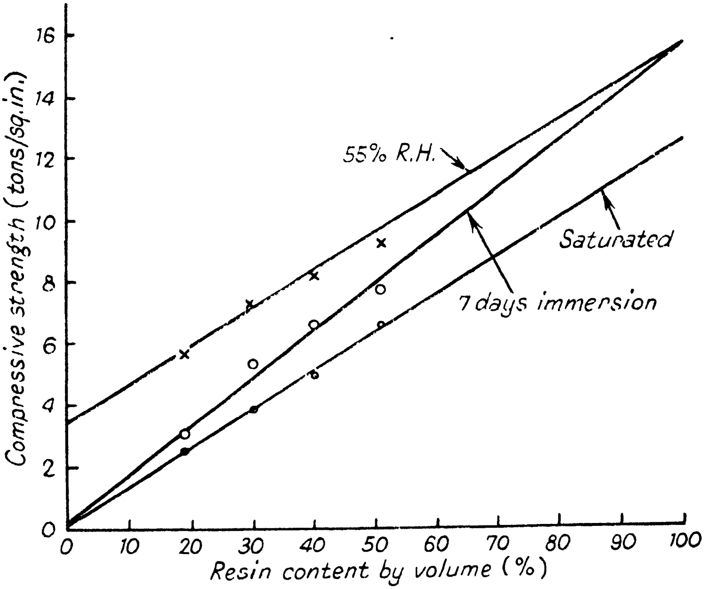


FIG. 99.—The compressive strength of fabric base laminates.[25]

New Developments in Resins for Laminated Materials

At one time or another most of the thermosetting resins have been used in the production of laminated and reinforced plastics. The melamine resins, which may conveniently be filled with macerated fabric or α-cellulose, have an excellent abrasion resistance. Further information concerning them has been given by Simmonds, Bigelow and Sherman.[26] Here, it is intended to deal with two types of resin which have a particular interest in relation to mechanical properties; the first concerns certain allyl plastics called "Columbia Resins" which have been described by Pechukas, Strain and Dial.[27] The second concerns the use of cellulose derivatives. Pechukas and his co-workers point out that their resins are, in certain of their properties, transitional between the thermosetting and thermoplastic groups. For example, they give insoluble products with excellent abrasion resistance (8 to 12 times that of methacrylate), and are able to polymerize from a liquid monomer to give a clear product. This reaction is a true polymerization and is not accompanied by the evolution of gases, though the usual slight shrinkage occurs. Such properties make it possible to form laminated structures at low pressures and the polymers have found particular application in the field of fibreglass laminates, though they can be used with many different reinforcing materials (Table LIV). The "Columbia Resins" described here are made from condensation products of allyl alcohol, phosgene and ethylene glycol.[28]

Laminates based on Cellulose Derivatives

A vital property of the reinforcing material is that of increasing the strength of the plastic under tension and impact,[12] but it is not necessary to use only the relatively weak phenolic materials as the plastic base in laminates, and recently Eurenius *et al.*[29] have described the properties of laminates derived from cellulose acetate and ethyl cellulose. As with most cellulose plastics, the properties can be varied according to the quantity of plasticizer included in the cellulose base mixture, so the results are tabulated with hard and soft formulations (Table LV). The main advantages claimed for these materials are lower elasticity (greater flexibility) and higher impact strength than with laminates made with the same filler using a phenolic resin. It is also stated that the hot

TABLE LIV. PROPERTIES OF C.R. 39 LAMINATES FROM STANDARD A.S.T.M. TESTS AT 70° F.[27]

Material	Specific gravity	Tensile strength	Flexural strength	Flexural modulus	Compressive strength	Impact strength, notched Izod ft.-lb./in. of notch	Bonding strength
		lb./in.^{2}	lb./in.^{2}	lb./in.^{2}	lb./in.^{2}		lb./in.^{2}
Kraft paper:							
Longitudinal	1·387	21,600	22,600	1,190,000	31,400	0·91	255
Transverse	1·387	10,700	17,400	780,000	31,400	0·61	226
8 oz. duck:							
Longitudinal	1·369	9,000	14,100	420,000	29,200	3·2	429
Transverse	1·369	7,200	13,100	360,000	29,200	2·1	370
Mitscherlich paper:							
Longitudinal	1·414	25,600	25,800	2,090,000	29,200	1·1	166
Transverse	1·414	10,400	16,400	815,000	29,200	0·90	167
Fiberglass ECC—11—148:							
Longitudinal	1·736	37,800	24,600	1,480,000	48,000	25	286
Transverse	1·736	32,000	25,400	1,180,000	48,000	15·7	266
Cast C.R. 39	1·315	5,000–6,000	9,500	280,000-350,000	22,100	0·31	—

TABLE LV. MECHANICAL PROPERTIES OF REINFORCED CELLULOSE ACETATE AND ETHYL CELLULOSE COMPARED WITH A PHENOLIC GRADE C RESIN. REINFORCING MATERIAL 8 OZ. DRILL CLOTH, 30 PARTS TO 70 PARTS RESIN[29]

Material	Impact strength ft.-lb./in. notch edgewise	Flexural strength	Modulus of elasticity in flexure	Tensile strength	Modulus of elasticity in tension	Specific gravity
		lb./in.^{2}	lb./in.^{22} × 10^3	lb./in.^{2}	lb./in.^{2} × 10^3	
Cellulose acetate:						
Soft plastic ..	4	680	14	500	16	1·26
Soft laminate ..	7·3	1,600	41	4,300	79	1·31
Hard plastic ..	2·9	9,600	230	7,200	260	1·32
Hard laminate ..	5·5	10,400	260	8,040	390	1·33
Ethyl cellulose:						
Soft plastic ..	—	400	5·7	460	9	1·06
Soft laminate ..	5·8	1,900	62	2,940	59	1·16
Hard plastic ..	4·0	5,000	108	3,100	140	1·09
Hard laminate ..	5·4	5,900	150	5,370	337	1·13
Phenolic grade C ..	3·9	13,000	440	8,000	850	1·35

materials are readily drawn into complex shapes with inexpensive equipment. Cellulose thermoplastics may also be combined with other types of filler such as fibre-glass and asbestos cloth with characteristic variations in the product.

Fibre-Glass Laminates

The high tensile strengths attainable with glass fibres have already been mentioned (Chap. III) in connection with Griffith's theory of flaws in glass. As an example of these high strengths, recent figures given by Slayter[30] show the tensile strength of standard glass fibres in the thickness range 0·0007 to 0·0002 in. diameter to be about 300,000 lb./in.^{2} (approx. 21,000 kg./cm.^{2}), and experimental fibres have been produced with a tensile strength of 2,000,000 lb./in.^{2} The method used for measuring the properties of glass fibres is shown in Plate XVI. The strength of glass fibres tends to decrease after their formation, and it is important to treat them in such a way as to preserve their high strength; Slayter recommends that the fibres should be suitably lubricated before they are made into a fabric. Other ingredients, such as gelatin or starch, which can give a firmly adhering organic film when the fibre is subjected to suitable heat treatment, may be conveniently incorporated in the lubricant. Impregnation with resin and thin flock fibres follows. Adhesion between glass fibre and resin may also be improved by heating the glass at 400° F. for 2 hours to remove the adsorbed film of water.[31]

Many types of resins have been used for the purpose of making fibre-glass laminates, among the most popular being the allyl type plastics which lend themselves to manipulation at low pressure. Nevertheless, many of the outstanding mechanical properties of the fibre-glass laminates appear to be largely determined by the properties of the glass fibres. For instance, the measured tensile strength of the reinforced material has a linear dependence on the glass content[32] (Fig. 100), and, according to Preston,[33] the elastic modulus also depends mainly on the amount of glass fibres present. However, elasticity in particular directions may also be affected by varying the structure of the fabrics used; in typical cases ordinary woven all-glass fabrics give a modulus of 2 to $2\frac{1}{2} \times 10^6$ lb./in.,[2] but if the glass fibres are predominantly in the same direction a modulus of $4\frac{1}{2} \times 10^6$ lb./in.[2] can be reached.[30] Compression strength, on the other hand, is more sensitive to the firmness of the connection between the laminations, and can be strongly influenced by the addition of flock fibres to the resin[32] (Fig. 101). These results serve to indicate some of the strength properties shown by these materials, but it is also important to remember that, as with other laminated plastics, the strength

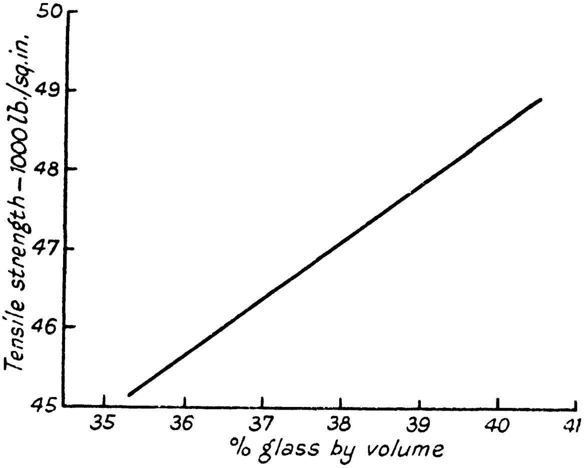


FIG. 100.—The tensile strength of a fibre-glass laminate.[32]

values will depend on the direction of the stress. For instance, Armstrong[34] reports that the tensile strength at 45° to the principal directions of the cross-stacked fibres is 30 to 40 per cent lower than the corresponding "with grain" values. This factor will naturally also play a part in compression tests, where again, according to Armstrong, failure takes place in "diagonal shear."

An important consequence of the vast increase in the tensile strength of glass fibres without any comparable change in the modulus of elasticity is that a material in which these properties predominate has a very high capacity for absorbing energy. As an approximate illustration we may consider a glass with a bending or tensile strength of, say, 1,000 kg./cm.^{2} and a modulus of elasticity of 700,000 kg./cm.^{2} Such a material would have a maximum strain energy of approximately 0·7 kg./cm./c.c., a value in accordance with the brittle behaviour of glass; but with a fibre of the same elastic modulus and a tensile strength of 20,000 kg./cm.^{2} the maximum strain energy rises to 300 kg./cm./c.c. It is, therefore, in accordance with approximate theoretical considerations based on the known properties of the glass fibre that most fibre-glass laminates have a characteristically high impact strength.

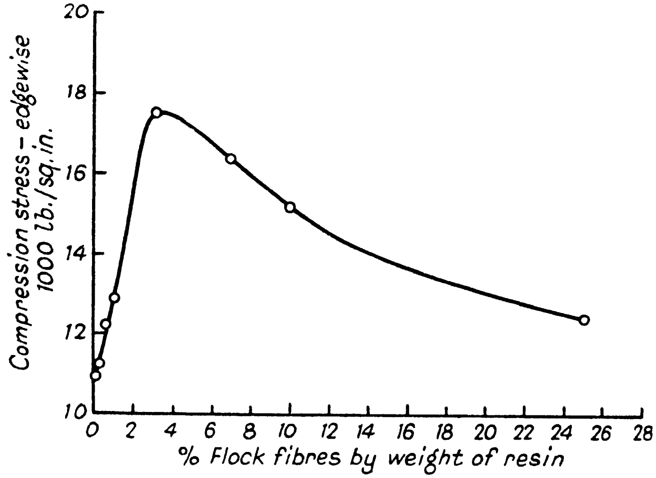


FIG. 101.—The effect of flock fibres on the compressive strength of a fibre-glass laminate.[32]

In Tables LVI and LVII some figures, taken from the work of Field,[13] are tabulated for the impact and tensile properties of phenolic laminates. Examples are included of high-strength paper, TABLE LVI. IZOD NOTCHED IMPACT STRENGTH OF LAMINATED PHENOLIC RESINS[13]

Reinforcing material	Edgewise			Facewise		
	Low temperature (− 70° F.) ft.-lb./in. notch	Room temperature (+ 76° F.) ft.-lb./in. notch	High temperature (+ 160° F.) ft.-lb./in. notch	Low temperature (− 70° F.) ft.-lb./in. notch	Room temperature (+ 76° F.) ft.-lb./in. notch	High temperature (+ 160° F.) ft.-lb./in. notch
Paper:						
With grain ..	1·0	1·0	1·0	4·0	4·0	4·0
Across grain..	1·0	1·0	1·0	4·0	4·5	4·0
Asbestos:						
With grain ..	2·0	2·0	3·0	4·0	4·0	5·0
Across grain..	3·0	2·0	3·0	5·0	5·0	5·5
Glass:						
With grain ..	33·5	22·0	20·0	29·0	23·0	27·5
Across grain..	31·0	22·5	20·5	31·5	32·5	31·0

asbestos and glass fillers, and the results enable a comparison to be made of the contributions of different reinforcing materials. Although the characteristically high tensile and impact strength of the fibre-glass plastics depend largely on the properties of the glass fibres, other aspects of the strength of these materials are much more dependent on the type of resin used. This problem has been investigated by Strain[35] for a particular heat-cleaned fibre-glass material laminated with different types of allyl resin. His results (Figs. 102 and 103) indicate a relationship between both the compressive and bending strength (modulus of rupture) of the laminate and the same properties in the resin used. For elasticity and tensile strength there is a smaller range of variation in the properties of the fibre-glass laminates with a variation in the resin (Figs. 104 and 105). These results compare interestingly

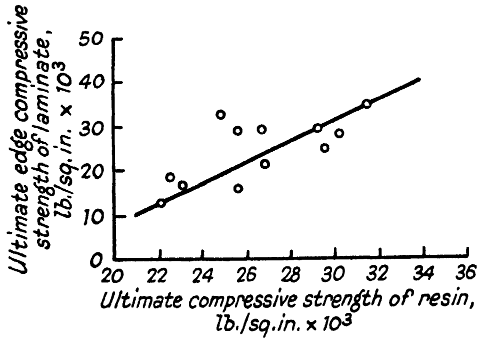


FIG. 102.—The relation between the compressive strength of a fibre-glass laminate and that of the resin used.[35]

TABLE LVII. TENSILE PROPERTIES OF REINFORCED PHENOLIC LAMINATES[13]

Material	Low temperature (− 70° F.)				Room temperature (+ 76° F.)				High temperature (+ 160° F.)			
	Ultimate strength	Yield strength	Secant modulus 10^6	Elongation	Ultimate strength	Yield strength	Secant modulus 10^6	Elongation	Ultimate strength	Yield strength	Secant modulus 10^6	Elongation
	lb./in.^{2}	lb./in.^{2}	lb./in.^{2}	%	lb./in.^{2}	lb./in.^{2}	lb./in.^{2}	%	lb./in.^{2}	lb./in.^{2}	lb./in.^{2}	%
Paper:												
With grain:												
Maximum ..	27,450	19,300	2·760	0·0	21,000	11,270	1·610	1·5	13,400	6,800	0·971	1·5
Minimum ..	26,750	18,900	2·700	0·0	20,500	11,240	1·605	0·5	10,520	5,110	0·730	1·0
Across grain:												
Maximum ..	24,800	18,100	2·590	0·0	20,830	11,860	1·694	1·0	12,920	6,590	0·941	1·0
Minimum ..	24,150	17,700	2·530	0·0	19,470	11,260	1·609	0·5	10,570	5,930	0·847	1·0
Asbestos:												
With grain:												
Maximum ..	20,800	14,200	2·029	1·5	19,550	12,920	1·845	1·0	10,550	7,120	1·017	1·0
Minimum ..	18,730	13,120	1·874	1·5	18,800	11,970	1·710	0·5	9,910	7,010	1·001	0·5
Across grain:												
Maximum ..	16,680	11,940	1·706	1·0	15,250	10,370	1·482	1·0	11,250	7,340	1·049	1·0
Minimum ..	16,180	11,680	1·669	0·5	14,800	10,250	1·465	0·5	10,590	7,100	1·014	0·5
Glass:												
With grain:												
Maximum ..	48,200	15,900	2·271	—	39,600	17,340	2·477	—	30,250	16,300	2·329	0·0
Minimum ..	44,700	13,850	1·979	0·0	39,400	16,150	2·307	—	28,250	16,280	2·326	0·0
Across grain:												
Maximum ..	45,900	14,480	2·070	—	30,600	19,810	2·830	0·0	26,700	16,150	2·307	0·0
Minimum ..	45,100	14,000	2·000	0·0	29,500	18,100	2·586	0·0	22,750	16,080	2·297	0·0

with those of Pepper *et al.*,[21, 22] who found that the compressive strength of paper laminates with more than 20 per cent resin content was that of the resin.

The valuable properties of the fibre-glass laminates undoubtedly

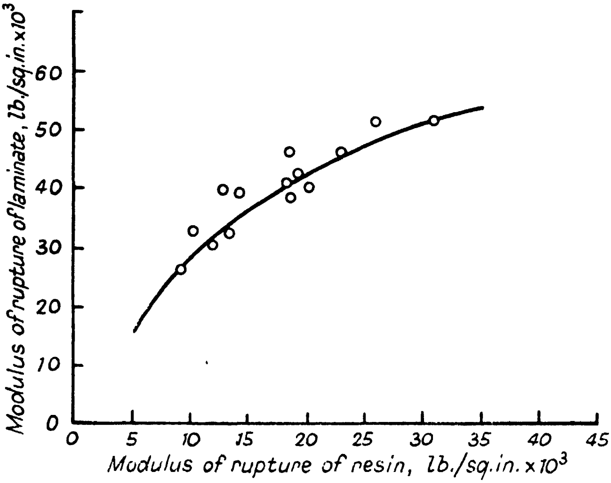


FIG. 103.—The relation between the bending strength of a fibre-glass laminate and that of the resin used.[35]

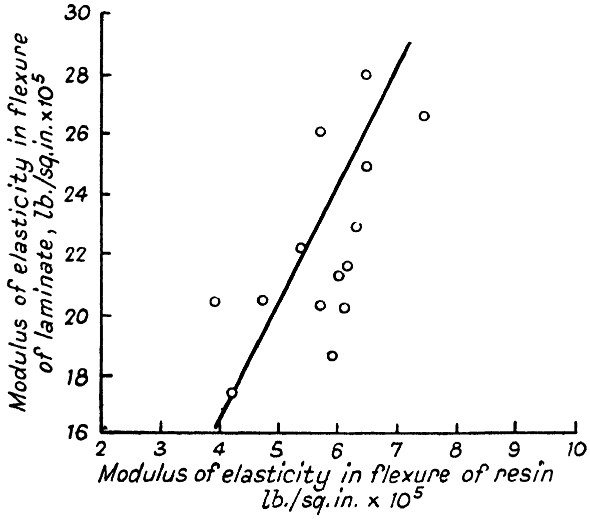


FIG. 104.—The relation between elastic modulus of a fibre-glass laminate and that of the resin used.[35]

hold out the possibility of new engineering developments, particularly where high strength and low density are desired. At present, one difficulty lies in the comparatively high cost of the fibre-glass itself, and for this reason mixed glass-cotton cloths are often used for reinforcement, giving laminates with intermediate properties.

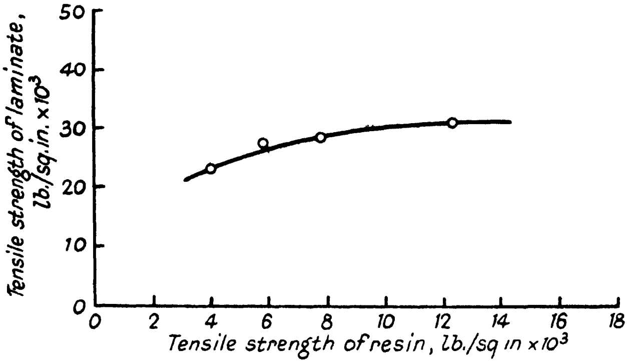


FIG. 105.—The relation between the tensile strength of a fibre-glass laminate and that of the resin used.[35]

Laminated Glass

This material has already been mentioned in connection with the problem of the bending and breaking of a complex beam[2]; however, these properties actually involve what are among the points of weakness in the material. Actually, the lamination is introduced simply to overcome the dangerous splintering effects which are characteristic of the breaking of glass. The properties of laminated glass are such that under a light blow it may be cracked but the assembly remains a coherent whole. However, if the energy of the blow is increased a point is reached where the glass may be penetrated, or, more commonly, broken up into a number of large pieces. Under these circumstances the breaking of the glass may be described as "brittle," and it is upon the property of brittleness that the testing of laminated glass is generally based. In practice, the energy required to bring about a 50 per cent probability of brittleness may be four or five times as large as that required to crack the glass. The measurement of the energy required to cause brittleness in this material is, therefore, of some general interest in that the main part of the energy involved is concerned with the tearing and breaking up processes after the formation of the first cracks. The results are also remarkable in that they illustrate the possibility of drastic *positive* velocity sensitivity with complex materials.

Before presenting the experimental results in detail a short digression is necessary on the methods available for estimating the impact behaviour of laminated glass. Only one impact can be made on each specimen since the glass will invariably be cracked by any blow giving a significant probability of brittleness, and further tests cannot be made on such a sample. Measurements are therefore carried out by subjecting groups of similar test pieces to a specified impact and observing the number of glasses which are broken up and the number which remain coherent. By making several such experiments it is possible to plot a curve showing the probability of brittleness in any particular circumstances (Fig. 106).[2] However, in this type of experiment both the energy and velocity of impact are changed, and greater interest attaches to results in which one of these quantities is kept constant and the other varied. For this purpose two courses are open. Either a series of glasses may be broken with the same energy of impact and different velocities (Fig. 107), or different balls (or bolts) may be dropped at a particular velocity to give curves showing the variation in the probability of brittleness with energy of impact at a particular velocity (Fig. 108). However, both these methods of experimentation give the same result with regard to the effect of varying velocity on the probability of brittleness with

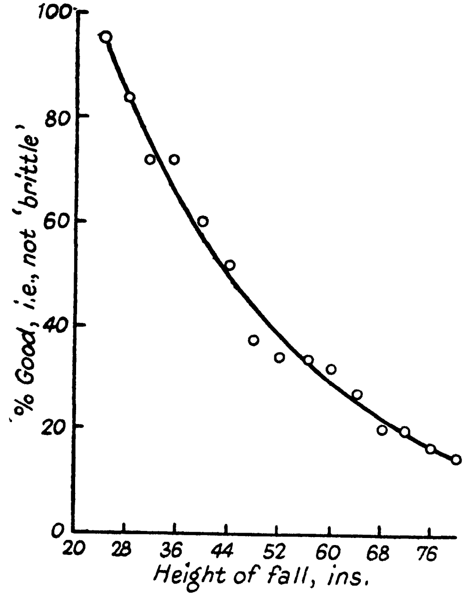


FIG. 106.—The effect of the energy of impact (height of fall) of the striker on the probability of brittleness in laminated glass.[2]

laminated glass, namely, the energy required to give a particular probability of the glass being broken up or penetrated increases as the velocity is raised, i.e. the material shows *positive* velocity sensitivity.

The drastic character of the effect may be seen from the fact

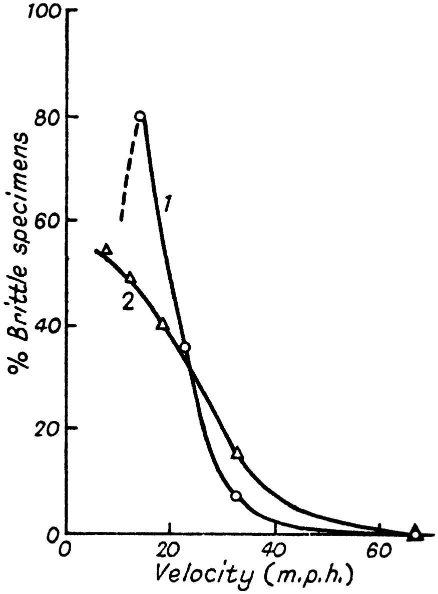


Fig. 107.—The effect of the velocity of impact on the probability of brittleness in laminated glass. All experiments carried out at constant energy of impact.[2]

that the energy required to produce a particular probability of brittleness increases about three times in the velocity range 11 to 67 m.p.h. A possible reason for this effect is suggested by the photographs in Plate XV. At the highest velocities the cracking or powdering is largely confined to the area around the point of contact and the impact stresses are not carried out to the edge of the glass along the whole length of the radial cracks. In such circumstances the glass is not readily broken up. For practical purposes this positive velocity sensitivity with laminated glass has an obvious value in connection with the use of the material in automobile windscreens, when impact in the velocity range 30 to 60 m.p.h. has to be considered. Indeed, the behaviour of laminated glass compares very favourably in this respect with that of toughened glass with its strong negative velocity sensitivity (Fig. 68), and the American practice of specifying laminated glass only for windscreens seems justified. In any case, the tests laid down in B.S.S. 857: 1939 would appear to be somewhat misleading (though not therefore unsuitable for their purpose) in that laminated glass is tested at the velocity at which it is weakest, and toughened glass at the velocity at which it is strongest. However, these results are mainly of interest in illustrating the wide possible variability of impact strength with velocity among complex materials, and underline the need for comparing the behaviour of two materials within the velocity range which they will be expected to meet in service. The rather surprising nature of the observations also makes it reasonable to assume that many useful possibilities inherent in complex materials still remain to be understood and applied.

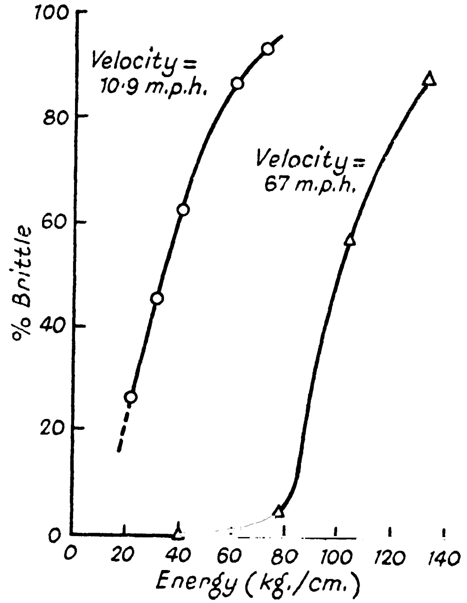


FIG. 108.—The effect of changing the energy of impact on the probability of brittleness in laminated glass. Experiments carried out with different strikers at the same velocity.

Note. The experiments described above were carried out with laminated glass, having a cellulose acetate interlayer. It should be noted that this material is now substantially displaced by polyvinyl butyral which has the advantage of a higher impact strength. However, although the reality of this improvement is not in doubt, the writer is not aware of any measurements of the impact strength of this type of laminated glass which are satisfactory from the statistical point of view.

REFERENCES—VII

(1) JACOBI, H. R.: *Kunststoffe*, **32** (1942), p. 1.

(2) HAWARD, R. N.: *J. Soc. Glass Tech.*, **28** (1944), p. 133.

(3) WATKINS, G. B.: *Glass Ind.*, **20** (1939), p. 448.

(4) *Brit. Plast.*, **16** (1944), p. 63.

(5) MCCRAIG, D. W., MCINTIRE, O. R.: *Mod. Plast.* (March 1945), p. 106.

(6) RHEINFRANK, G. B., NORMAN, W. A.: *Mod. Plast.*, Overseas edition (July 1945), p. 35.

(7) MEYER, L. S., CASE, S. C.: *Mod. Plast.*, Overseas edition (July 1945), p. 44.

(8) LINCOLN, J. D. (Jnr.): *Mod. Plast.*, Overseas edition (July 1945), p. 40.

(9) GARRARD, A.: *Brit. Plast.*, **18** (1946), pp. 380, 451.

(10) TIMOSHENKO, S.: *The Strength of Materials*, 2nd edition, Pt. II, p. 413 (Macmillan & Co., 1941).

(11) CALDWELL, L. E.: *Mod. Plast.* (August 1943), p. 82.

(12) DE BRUYNE, N. A.: *Roy. Aeronautical Soc. J.*, **41** (1937), p. 523.

(13) FIELD, P. M.: *Mod. Plast.* (August 1943), p. 91.

(14) BROWN, D. W.: *Plastics*, **8** (1944), pp. 177–86.

(15) FULLER, F. B.: *Mod. Plast.* (June 1943), p. 96.

(16) FIELD, P. M., SANG, H.: *Mod. Plast.* (October 1943), p. 107.

(17) CARSWELL, T. S., TELFAIR, D., HASLANGER, R. U.: *Mod. Plast.* (July 1942), p. 65.

(18) BROWN, W. J.: *Trans. Inst. Plast. Ind.* (1944), p. 112.

(19) YARSLEY, V. E.: *Plastics Applied*, Section IV, p. 437 (National Trade Press, 1945).

(20) BARBER, R. W.: *Paper Trade Journal*, TAPPI Section 120 (1945), pp. 190–3.

(21) COX, H. L., PEPPER, K. W.: *J. Soc. Chem. Ind.*, **63** (1944), pp. 150–4.

(22) PEPPER, K. W., BARWELL, F. T.: *J. Soc. Chem. Ind.*, **63** (1944), pp. 321–9.

(23) NELSON, D.: *Gen. Electric Review*, **46** (1943), p. 483.

(24) CROUP, A. H.: *Paper Trade Journal*, TAPPI Section 118 (1944), pp. 43–6.

(25) BARWELL, F. T., PEPPER, K. W., HALE, D. K.: *J. Soc. Chem. Ind. Trans.*, **65** (1946), p. 153.

(26) SIMONDS, H. R., BIGELOW, M. H., SHERMAN, J. V.: *The New Plastics*, p. 53 (D. Van Nostrand & Co., 1945).

(27) PECHUKAS, A., STRAIN, F., DIAL, W. R.: *Mod. Plast.* (June 1943), p. 101.

(28) SHELL PETROLEUM CO. (Private communication.)

(29) EURENIUS, C. W., HECHT, R. H., KOCK, W., MALPAS, H. C.: *Ind. Eng. Chem.*, **37** (1945), p. 959.

(30) SLAYTER, G.: *Mod. Plast.* (May 1944), p. 100.
(31) SLAYTER, G.: *Ohio State Univ. Expt. Sta. News*, **16** (1944), No. 4, pp. 3–8.
(32) KEMMER, P. H.: *Mod. Plast.* (May 1944), p. 89.
(33) PRESTON, F. W.: *Brit. Plast.*, **16** (1944), p. 440.
(34) ARMSTRONG, C. W.: *Iron Age*, **152** (1943), p. 51.
(35) STRAIN, F.: *Mod. Plast.* (August 1944), p. 97.

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